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CHEMISTRY

FOR STUDENTS

BY

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PREFACE.

This little book is intended to supply to Students of Chemistry an outline of the most interesting and useful facts pertaining to the Science, and of the most important ideas which have been got from a study of those facts.

The method of exposition differs from that which is adopted in most other treatises of Chemistry; for I describe and compare individual facts, so as to lead the mind of the reader towards general principles, instead of stating the general principles first and then proceeding to illustrate them by details.

The book is intended for the use of beginners in Chemistry, and also of Students who, having made some progress in the Science, wish to have an outline of the chief facts and theories of mineral and of organic Chemistry. Those who wish to proceed further and to obtain full particulars of any one part of the subject, will need to consult such books as Gmelin's Handbook, Watts's Dictionary, Miller's Elements, Gerhardt's Traité de Chimie organique, or Kekulé's admirable Lehrbuch der organischen Chemie. It is not intended as a substitute for *vivâ voce* and experimental teaching, but rather as a guide and aid

to Students and Teachers. A judicious Teacher will amplify the brief explanations and descriptions which I give; and will show experimentally the reactions and transformations which I mention. A Learner who wants to recall to mind what he has seen and heard may refer to the book for the substance of it.

The absolute 'volume' which I have for many years adopted in my classes is here employed in the calculations relating to gases. The knowledge of this absolute volume is of value to Learners, because it leads them easily from a class of facts to an important general conclusion, and it supplies to Chemists a ready means of calculating the weight of any given measure of gas or vapour. This absolute volume is in round numbers 11.2 litres, which is the bulk of one gramme of hydrogen, of sixteen grammes of oxygen, of fourteen grammes of nitrogen, &c., at the normal temperature and pressure; in fact the bulk of that quantity of any one of those gases which weighs as many grammes as there are units in the number expressing its atomic weight. Students will do well to work out the answers to the questions appended to the first few chapters, and thereby to practise themselves in using the elementary facts of Chemistry.

Among the additions which have been made to the former editions, I may mention the following as amongst the most important:—

1st. Tables of acids, bases, sulphides, salts, &c.

2nd. Diagrams explanatory of the proportions of combination by volume and by weight.

3rd. Explanations respecting the atomic theory and the replacing value of atoms, &c.

4th. Chapter on Naphthalene and Anthracene.

5th. Occasional use of explicit formulæ describing atomic arrangement.

I have also, more systematically than before, described hydrogen salts by names analogous to those applied to other salts.

This last edition has been revised by my friend Mr. Atkinson, to whom I owe some valuable suggestions respecting the arrangement of that part of the book which treats of organic compounds.

ALEX. W. WILLIAMSON.

UNIVERSITY COLLEGE, LONDON,
April, 1873.

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INORGANIC CHEMISTRY

INTRODUCTION.

The science of Chemistry is generally considered to date from the discovery of the nature of combustion. Lavoisier shewed that when a substance is burnt in the air, combination takes place between that substance and a constituent of the air, and something is formed by the combustion which can by suitable means be collected and examined. In no process of combustion is matter destroyed, for the materials employed weigh exactly as much as the product formed by their combination.

Thus mercury can be made to combine by a sort of combustion with a constituent of the air (called oxygen), and the compound thus formed (called mercuric oxide) weighs exactly as much as the mercury and the oxygen which were consumed in making it.

We are accustomed to say that the mercuric oxide *contains* mercury and oxygen; for 2 grammes of oxygen and 25 grammes of mercury are used to make 27 grammes of mercuric oxide; and we can get 2 grammes of oxygen and 25 grammes of mercury from 27 grammes of the oxide. Weight is, however, the only property in which the compound is identical with its constituents; and it is a characteristic of chemical combination that substances acquire new properties on combining with one another, their weight remaining unchanged. In order to decide whether two substances known to be intimately mixed with one another

are chemically combined or not, it is necessary to ascertain whether each of the substances has got in that mixture the same properties which it has by itself.

Thus air is known to contain oxygen and nitrogen intimately mixed; but we know that the oxygen is not chemically combined with nitrogen, because the oxygen in the air has the same properties as oxygen by itself, and the nitrogen in the air has the same properties as nitrogen by itself. We know several compounds of oxygen and nitrogen, but each of them has got peculiar properties of its own, different from those of free nitrogen and of free oxygen.

A careful examination of numberless processes of combination and of decomposition has shewn that all kinds of matter known to us on the surface of the earth are composed of a comparatively small number of elements. Thus a piece of white marble can be decomposed into carbonic acid and lime. The first of these can be made from carbon and oxygen, the second from calcium and oxygen. As neither carbon, oxygen, nor calcium can be decomposed so as to yield other substances, they are accordingly the elements of the marble. Pure white sugar can be burnt, and no other products are formed than carbonic acid and water, and these substances are known to consist of carbon, oxygen, and hydrogen. The weight of oxygen in the products is, however, greater than the weight of oxygen supplied during combustion. From these facts we infer that sugar contains the elements carbon, hydrogen, and oxygen.

Chemists have found that all well-known substances are built up of small particles of elementary matter. These particles can be united with one another and separated from one another; but in no case has any one of them been broken up into smaller particles, nor built up from smaller ones. They are accordingly called atoms. The absolute weights of atoms have not yet been ascertained; but

chemists have proved that the atoms of hydrogen are lighter than those of any other element, and they have discovered how many times heavier each elementary atom is than an atom of hydrogen; thus we know how many times heavier an atom of carbon is than an atom of hydrogen; and the so-called 'atomic weight' of carbon is a statement of that ratio for carbon. In like manner we know how much heavier an atom of oxygen is than an atom of hydrogen. The atomic weight of each element is the ratio of the weight of its atom to that of hydrogen. These atomic weights have been found by comparing the different proportions in which different elements combine; but the evidence upon which they rest can only be understood by those who know accurately the particulars of the very numerous chemical processes from the comparison of which they are derived. It is worthy of remark that philosophers (such as Descartes) had supposed that matter must be built up of atoms, long before Chemistry gave a definite experimental basis to the idea.

The atomic theory as now used by chemists is a generalization of a well-established experimental fact. We assume that all substances are built up of atoms in the same sort of way in which every well-examined substance is found to be built up of atoms. It is a fact that carbon in those processes of chemical change which are accurately known has not been further divided than into particles twelve times as heavy as the smallest particles of hydrogen; and we assume that the same peculiarity of carbon must belong to it in those other compounds which are as yet little known to us, or are entirely unknown. When a chemist investigates any new compound of carbon, he has present to his mind the peculiarities which the element has been found to exhibit in its known compounds, and of them the atomic weight is one of the most important. The 'theory' leads him to

expect and to find many important truths which would escape notice if he did not look for them; and it is more and more trusted in proportion as it has been found to be a useful and faithful guide.

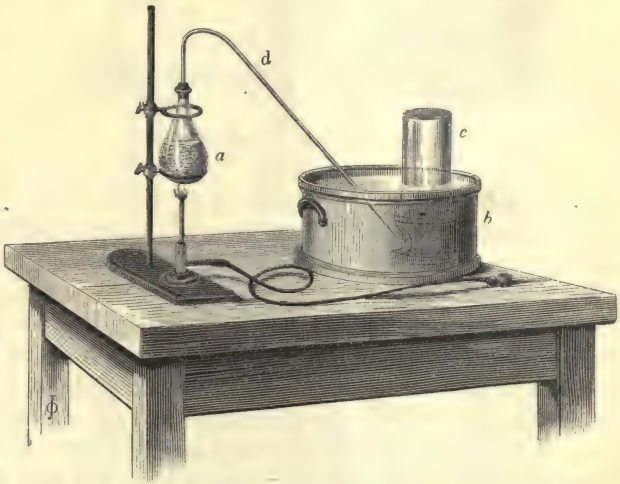
Respecting the constitution of the elementary atoms chemists know nothing. Whether each atom is in itself an aggregate of smaller particles, or whether it is in its very nature indivisible, are questions upon which the chemical theory has at present no hold. The chemist cannot break up an atom of carbon or of oxygen any more than an astronomer can break up the planet Mars or Jupiter. But there is no reason to suppose the elementary atoms incapable of subdivision by processes beyond our present reach, any more than there is reason to suppose that the planets might not be divided into smaller masses.

The atomic theory has been gradually consolidated and extended since Dalton established its first principles, and it has received particularly important additions of late years. Still it is but a beginning of a theory of chemical action. Many and many a patient and accurate worker and thinker will add his mite of facts and of ideas to the store, before the full and exact theory of the constitution of matter is established.

Every student of the science should strive to learn how to draw his ideas from experiment, the fountain-head of knowledge, and for that purpose he cannot do better than study how our present stock of ideas in Chemistry has been derived from experiment. He ought to accumulate more and more exact knowledge of the characteristic resemblances and distinctive differences among substances, stopping every now and then to look over the facts which he has accumulated, and to arrange them according to their resemblances. He will thus rise gradually to general theories in a sound and useful manner.

CHAPTER I.

1. Oxygen[a] is most conveniently prepared by heating pure potassic chlorate (chlorate of potash) in a glass flask



Preparation of Oxygen.—*a* Flask containing chlorate; *b* Griffin's trough; *c* jar collecting the gas; *d* bent tube.

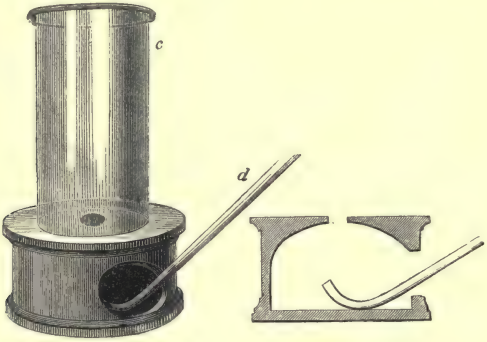
or tube. The salt first melts and then appears to boil, the bubbles which come off from it, being oxygen, are

[a] The symbol for the atom of oxygen is O, and the weight of the atom denoted by O is 16.

The formula of the molecule of oxygen is O^2.

The density of oxygen in the hydrogen scale is 16.

collected by displacement of water in a glass jar inverted in a pneumatic trough. The gas should be tested from time to

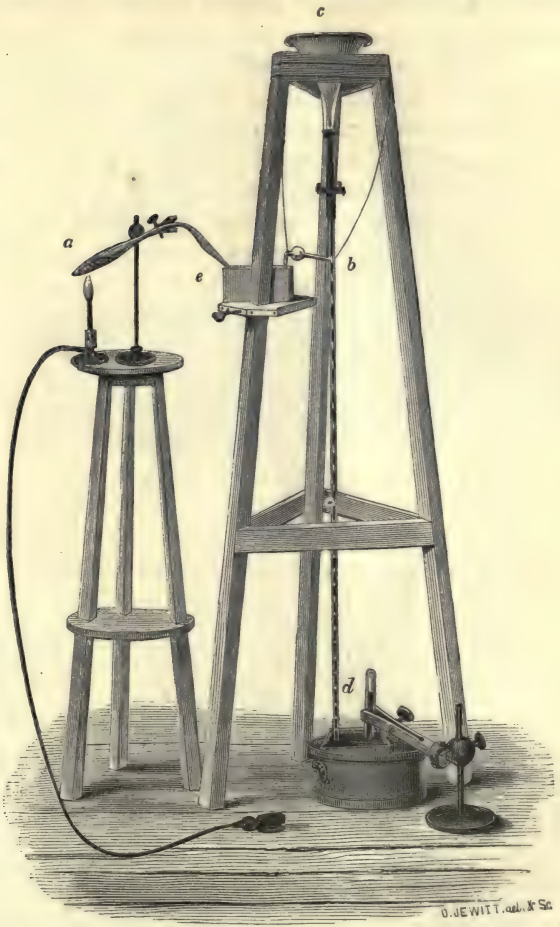


Enlarged view of jar with its support.

time as it comes off, by plunging into it the glowing end of a splint of wood. If the splint burst sharply into flame the gas may be assumed to be pure enough for most purposes. But if the purest obtainable oxygen be required, the operator ought to select a flask only just large enough to contain the quantity of chlorate which he wishes to decompose, and he ought to remove the air from the apparatus before decomposing the chlorate. For this purpose the Sprengel air-pump is employed as shewn in the annexed figure. The drops of mercury which fall successively down the tube of this instrument act like pistons, driving before them the air which enters at the horizontal tube *b*.

When all the air has been pumped out of the apparatus the action of the pump is stopped while heat is applied to the tube containing the chlorate. The oxygen finds a free outlet at the bottom of the pump, and is collected by displacement of mercury in a small jar, as by passing through water it would get contaminated by nitrogen which was dis-

solved in the water. Some persons recommend the addition



Sprengel's Air-pump attached to a small tube evolving Oxygen.—*a* Tube containing chlorate; *b* glass tube .002^{m} diameter; *c* funnel containing mercury; *d* tube for collecting gas; *e* trough of water surrounding an india-rubber joint.

of a little manganic peroxide to the chlorate which is to be heated, but although the chlorate is thus more rapidly decomposed, the advantage is dearly purchased, for the gas set free is liable to contain chlorine. Pure oxygen is completely absorbed by a solution of pyrogallic acid in strong potash, and whatever remains undissolved by this re-agent (excepting a trace of carbonic oxide) must be some other gas which had been mixed with the oxygen.

Potassic chlorate[b], if completely decomposed by heat, yields 39.183 per cent. of its weight of oxygen gas, the remaining salt being potassic chloride, a compound of potassium with chlorine. Some of the chlorate employed is however usually carried away by the oxygen in the form of spray, and thus escapes decomposition; and some oxygen is often retained in the form of potassic per-chlorate, a salt which requires for its decomposition a higher temperature than that at which the chlorate is decomposed.

When oxygen is wanted in very large quantities, it is more economically prepared by heating a mineral called 'Manganese.' The process is performed in a stone-ware retort similar to those used for making coal gas. The mineral consists of the metal manganese combined with oxygen, but the utmost heat is unable to drive off more than one-third of the oxygen contained in the pure mineral[c].

2. Oxygen is a component of atmospheric air, and can be prepared from it in a pure state. An experiment of Lavoisier's shews this result in a very interesting form. Mercury is boiled in a convenient vessel containing say 100 cubic centimetres of air, care being taken that no air shall escape. A red powder is formed by combination of some

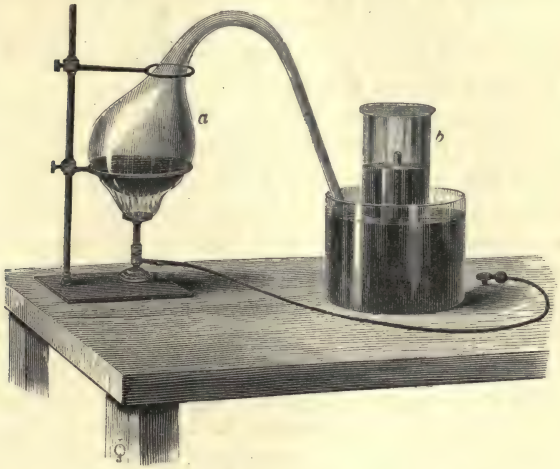
[b] A molecule of potassic chlorate is represented by the formula $KClO_3$. The decomposition which this salt undergoes is represented by the equation

$$KClO_3 = KCl + 3O.$$

[c] The action of heat upon the 'manganese' is represented by the equation

$$3MnO_2 = Mn^3O_4 + O^2.$$

of the mercury with oxygen, and if the process be allowed to continue about twelve days the mercury will absorb nearly



Lavoisier's Preparation of Oxygen from Air.—*a* Flask containing air and mercury and communicating with the air in the jar *b*.

all the oxygen contained in the air. If the oxygen were completely removed, the residual gas would measure rather less than 80 cubic centimetres; so that oxygen constitutes rather more than one-fifth of the volume of atmospheric air. A burning taper plunged into the residual gas goes out. While losing its oxygen the air has lost the power of supporting combustion. When the red compound of mercury and oxygen is heated to a temperature sufficiently above that at which it was formed, it is decomposed into metallic mercury and oxygen[d]; and if this oxygen be returned to the air from which it had been removed by the action of mercury, it restores to the air the power of supporting combustion.

[d] $HgO = Hg + O$.

3. Iron wire can be lighted in an atmosphere of oxygen, by fixing a piece of tinder to its end, and kindling it before it is put into the gas. The iron burns with great intensity, while white hot globules are formed at the end of the wire, and increase in size till they drop off. These globules consist of iron combined with oxygen[e].

Phosphorus also burns in oxygen with great intensity. A small piece of that substance ought to be carefully dried, and put into a little copper spoon. It can very easily be lighted by a match while still surrounded by air, and if then lowered into a jar of oxygen it immediately burns with far greater brilliancy and rapidity than in air, and gives off a dazzling light. A white powder called phosphoric acid is formed in this process, by combination of the phosphorus and oxygen[f]. When sulphur is burned in oxygen there is no solid or visible product formed, and the blue flame which is produced during the process is far less luminous than the white flame of the burning phosphorus. In proportion however as the combustion proceeds the oxygen disappears, and in its place is found a gas of an exceedingly powerful and well-known smell. This gas, called sulphurous acid, is a compound of sulphur and oxygen[g].

The combustion of charcoal affords another interesting instance of combination with oxygen. A piece of light wood charcoal should be selected for the purpose, and in proportion as it burns away, a gas is produced containing carbon combined with oxygen[h], and possessing feebly acid properties. This gas (called carbonic acid) is readily absorbed by caustic potash, and can thus be separated from oxygen.

Metallic sodium burns very vividly in oxygen, forming a white powder which can easily be dissolved in water with effervescence.

[e] $Fe^2 + 3O = Fe^2O_3$. [f] $P^2 + 5O = P_2O_5$. [g] $S + O^2 = SO_2$. [h] $C + O^2 = CO_2$.

4. In all these processes of combustion there are products formed which weigh exactly as much as the materials used in their formation; and in no case of combustion is there a destruction of materials. Every kilogramme of sulphur which is burnt takes up a kilogramme of oxygen, forming 2 kilogrammes of sulphurous acid; and if this sulphurous acid were collected, the sulphur could be recovered from it. In like manner every kilogramme of carbon fully burnt forms $3\frac{2}{3}$ kilogrammes of carbonic acid, by combining with $2\frac{2}{3}$ kilogrammes of oxygen, and both the carbon and oxygen can be got out of this compound by suitable processes.

But except in the one particular of weight, these products have different properties from the materials which formed them; and the object of chemistry is to explain the changes of property which substances undergo by acting on one another.

5. Oxygen is a colourless gas devoid of taste and smell. It is a little heavier than atmospheric air. It is 16 times as heavy as hydrogen at the same temperature and pressure, and is accordingly described as having a density equal to 16 when that of hydrogen is represented by unity. Air is only 14.45 times as heavy as hydrogen.

In the metrical system, which is the most convenient for calculations, the volume of a fixed weight of oxygen is thus stated: 16 grammes of oxygen measure 11.19 or very nearly 11.2 litres at 0°C, and 760 millimetres of mercury pressure. The same measure (11.2 litres) of water of the maximum density weighs nearly 700 times as much; so that under these conditions of temperature and pressure oxygen has about $\frac{1}{700}$ the density (or specific gravity) of water. In grains and cubic inches the same relation may be thus stated: 16 grains of oxygen at 0°C and 29.9 inches pressure measure 44.473 cubic inches. When 100 measures of oxygen are

measured off at 0°C and then heated to 1°C they become 100.3665, when heated to 2°C they become 100.7330, and so on, gaining .3665 for every degree rise of temperature counted from 0°C. It follows from this, that if 100 volumes of the gas were measured off at 15°C, and then heated to 16°C, the increase of volume would be found by the following proportion:

$$100 + 15 \times .3665 : 100 + 16 \times .3665 = 100 : x,$$

or $105.4975 : 105.8640 = 100 : x$, which gives us for the volume at 16°C, $x = 100.34$.

6. If oxygen were kept at the same temperature and subjected to greater and greater pressure, it would diminish in volume in proportion to the increase of pressure. Thus if a litre of oxygen were measured off in stormy weather while the barometer stood at 700 millimetres, and then put aside and measured at the same temperature, but after the barometer had risen to a height of 750 millimetres, it would be found to have diminished in volume in the proportion of 75 to 70, and would only measure 0.933 of a litre. It is convenient to state this law thus: the density of oxygen at a given temperature is proportional to the pressure to which it is subjected. By exposure to a pressure of about 300 atmospheres, oxygen has been reduced to $\frac{1}{300}$ of its ordinary volume, but further pressure did not appear to produce a corresponding diminution of volume.

When oxygen is heated and yet not allowed to expand, it presses against the sides of the vessel in which it is contained with an amount of force which increases, with rise of temperature, in the same proportion in which expansion takes place under constant pressure. Thus if we measure out 1 litre of oxygen at the temperature of 0°C, and if while heating the gas to 15°C we wish to prevent it from expanding, we must increase the pressure upon it in round numbers in the proportion of 273 to 273 + 15. If at

the commencement of the experiment a barometer in the same room stood at a height of 760 millimetres, the litre of oxygen was under a pressure of the air equal to a column of mercury 760 millimetres (or 30 inches) high; and the pressure required to prevent the air from expanding whilst it is being heated is found by the proportion : $273 : 288 = 760 : x$ which gives us $x = 801.7$; so that we must increase the atmospheric pressure by an amount equal to a column of mercury rather more than 41 millimetres high to keep our oxygen to the bulk of a litre when it is heated from 0°C to 15°C.

7. Oxygen is absorbed by venous blood, and imparts to it a bright red colour. Carbonic acid is given off at the same time that the oxygen is absorbed. The respiration of animals takes place quite freely in oxygen, but the pure gas has too stimulating an action, and soon disturbs the regular working of the process, by inducing too rapid an oxidation for the requirements of the system.

Fresh leaves of plants give off oxygen, when placed in the sunshine, in contact with carbonic acid.

8. Ozone. Under particular conditions, the oxygen which is given off in the decomposition of dilute sulphuric acid by the galvanic battery is found to have a sickly smell, owing to the presence in it of a substance of more actively oxidizing properties than ordinary oxygen. The same substance is said to be formed by the action of an electrical brush discharge on pure oxygen. It is destroyed by passing the oxygen containing it through a glass tube heated to redness by a lamp; and by contact with india-rubber, or cork, or any other vegetable or animal substance, it is immediately destroyed, producing water and carbonic acid, by the oxidation of the hydrogen and carbon of the vegetable substance. Even metallic silver is transformed into an oxide by contact with this powerful substance.

Until the substance is isolated and fully examined, we cannot with certainty pronounce upon its nature, but some chemists are of opinion that it is nothing else than oxygen which has undergone a change of properties.

The very great majority of the compounds of oxygen hold that substance so firmly that it cannot support combustion so easily as in the free state; but there are some compounds of oxygen in which it has more active combining tendencies than in the free state, and some of them are known to produce effects similar to those by which ozone is usually tested. The atmosphere is said by some persons to contain ozone, when paper moistened with potassic iodide and starch turns blue by contact with it.

Appendix to Chapter I.

PROBLEMS.

1. What weight of oxygen is contained in one kilogramme of potassic chlorate?

2. 100 litres of oxygen at 0°C, and 760 millimetres barometric pressure, are wanted. How much potassic chlorate must be decomposed for its production, assuming that all the oxygen can be expelled from the salt?

3. 30 litres of oxygen were measured off at 15°C. What would be the volume of the gas at 0°C, the pressure remaining unchanged?

4. What weight of oxygen is required to fill a globe of 13 litres capacity, at the temperature of 12°C, and at the normal barometric pressure?

5. 10 litres of oxygen are measured off at 14°F. Required the volume of the gas at 15°C.

6. 230 cubic centimetres of oxygen are measured off at 14°C and 740 millimetres mercurial pressure. Required the volume of the gas at the normal temperature and pressure (0°C and 760 millimetres).

7. 43 grammes of oxygen were measured off at the normal pressure, and at a temperature such that their density was 18. Required the volume of the gas in litres, and the temperature at which it was measured.

8. A flask is filled with oxygen at 0°C, at 760 mm. pressure, and the flask is then tightly corked. The flask would burst if exposed to an outward pressure of 1500 mm. At what temperature would the oxygen exert this pressure, assuming the capacity of the flask to remain unaltered?

9. A litre of oxygen is confined in a glass flask at 10°C by the atmospheric pressure, added to that of a column of mercury 60 millimetres high. The flask must be heated to 300°C, without any increase of volume taking place in the oxygen. How high must the column of mercury then be which presses on the gas, supposing the atmospheric pressure to remain constant at 760 mm.?

10. A litre of oxygen is required of the density of 100 at 0°C. What weight of potassic chlorate must be used for its preparation, and what total pressure must be applied to it?

CHAPTER II.

9. Hydrogen[i] is most conveniently prepared by pouring upon metallic zinc a very acid salt called hydric sulphate, previously mixed with three or four times its volume of water[j]. The gas comes off from the surface of the zinc and can be collected in the same way as oxygen. The process by which it is here given off is illustrative of the chemical nature of hydrogen, for the hydric sulphate consists of hydrogen combined with sulphur and oxygen, and the metal zinc actually pushes the hydrogen out of this compound and takes its place[k]. It will be seen that there are many other cases of a metal combining with the same elements as hydrogen. If a sufficient quantity of zinc be used to expel all the hydrogen from the sulphate employed in the experiment, it will be found that the liquid left in the bottle consists of a solution of a compound of zinc with sulphur and oxygen, called zinc sulphate. This salt can be obtained in the form of beautiful white crystals, by carefully evaporating off the water until the solution, on cooling, deposits some of the substance dissolved in it. Iron wire also dissolves in dilute hydric sulphate, giving off hydrogen gas, and forming a crystallizable salt, called ferrous sulphate, consisting of iron combined with

[i] Atomic symbol H = 1. Molecular formula H^2. 11.19 litres of hydrogen weigh one gramme at 0°C, and an atmospheric pressure equal to 760 millimetres of mercury (32°F and 30 inches).

[j] This acid salt is often called sulphuric acid, a name which belongs to another compound obtained from it by the removal of the elements of water.

[k] $H_2SO_4 + Zn = ZnSO_4 + H^2$.

sulphur and oxygen[l]. But the hydrogen prepared by the use of iron, usually has an unpleasant smell, owing to the presence in it of a compound of carbon and hydrogen. Sulphur, phosphorus, and arsenic are not uncommon impurities in hydrogen, and the vapour of water necessarily accompanies it from the generating flask.

10. To remove these impurities the gas should be passed slowly through a tube containing pieces of pumice-stone moistened with a solution of argentic nitrate, which keeps back the sulphuretted hydrogen, phosphuretted hydrogen, and arseniuretted hydrogen; and through a second tube containing pumice moistened with strong oil of vitriol, which absorbs the moisture in the gas.

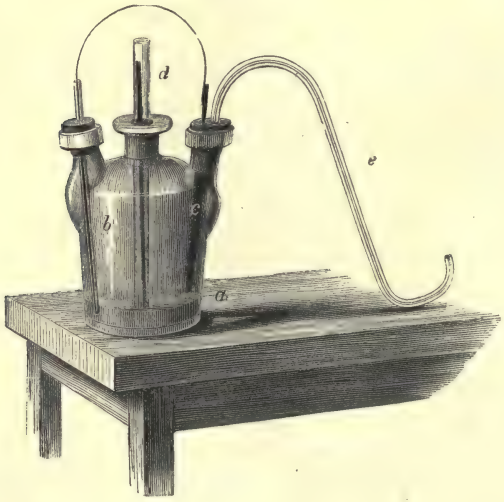
It has been noticed that hydrogen on passing through concentrated oil of vitriol acts upon it like any other metal, forming sulphurous acid, and a compound of the sulphate with two molecules of water, unless the liquid be kept at 0°C. Thus, to dry the hydrogen completely, it is advisable to pass it through a bottle containing phosphoric acid.

Many metals are capable of decomposing water and liberating hydrogen from it, just as zinc and iron decompose hydric sulphate[m]; but some of these metals, such as potassium and sodium, are too expensive to be used in the common preparation of the gas; and others, such as iron[n], only decompose water at high temperatures, which it is not always convenient to employ.

In order to prepare hydrogen in small quantities free from any other impurity than moisture, an apparatus of the construction represented in the annexed woodcut is used with advantage. It contains the same materials as those employed in the process just described, but the metallic zinc is dissolved in mercury before acting on the hydric sulphate. The action

[l] $Fe + H_2SO_4 = FeSO_4 + H^2$. [m] $Na^2 + 2H_2O = 2NaHO + H^2$.
[n] $3Fe + 4H_2O = Fe^3O_4 + 4H^2$.

continues as long as mercury containing zinc is connected by a wire with the platinized silver plate *c*, and it ceases as soon as that contact is interrupted. The plate of platinized silver remains unchanged, and the bubbles of hydrogen are given off from its surface. The impurities contained in the



Apparatus for evolving pure Hydrogen.—*a* Mercury containing metallic zinc; *b* copper wire surrounded by glass tube; *c* coiled plate of platinized silver; *d* wide tube dipping into the mercury containing strip of zinc; *e* tube for escape of hydrogen.

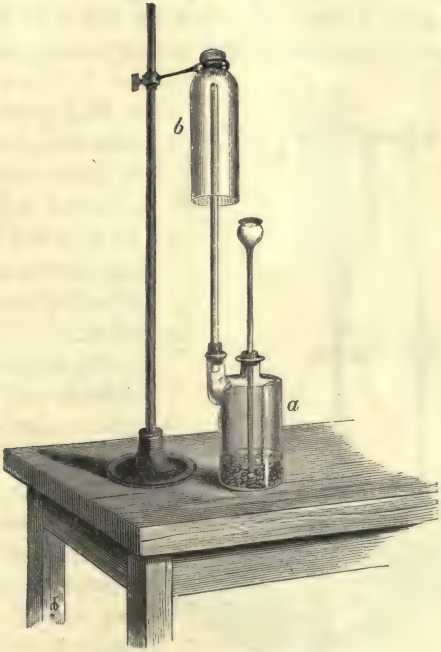
metallic zinc, which in the ordinary form of apparatus would pass over into the hydrogen, are here left behind, as they are not soluble in the mercury.

The theory of this instrument will be understood by those who are acquainted with the laws of galvanic action.

11. Hydrogen, when collected pure, does not explode, but burns quietly when ignited. Mere traces of oxygen can

be discovered in it by a diminution of the volume of the gas subjected to the prolonged action of electric sparks in a tube over mercury.

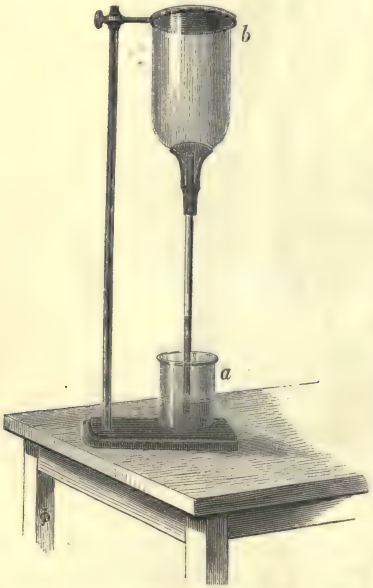
Hydrogen is the lightest substance known, 1 gramme of it measures exactly as much as 16 grammes of oxygen, viz.



' *a* Bottle for evolving hydrogen; *b* bell-jar for collecting hydrogen by displacement of air.

11,19 litres, so that oxygen is 16 times as heavy as hydrogen. One grain of hydrogen at 0°C and 760 millimetres pressure measures 44.473 cubic inches. Hydrogen has less than $\frac{1}{14}$ the density of air ($\frac{1}{14.45}$), and it accordingly tends

to rise to the top of any vessel containing air. Thus a glass bell-jar, suspended with its mouth downwards, may be filled with hydrogen by leading a rapid current of the gas up to the top of the bell-jar, by a tube, as shewn in the annexed figure. That the hydrogen remains for a short time in the bell-jar can be proved by passing a lighted taper up into it, when the taper is extinguished but sets fire to the hydrogen. Its extreme lightness makes this gas particularly suitable for filling balloons.



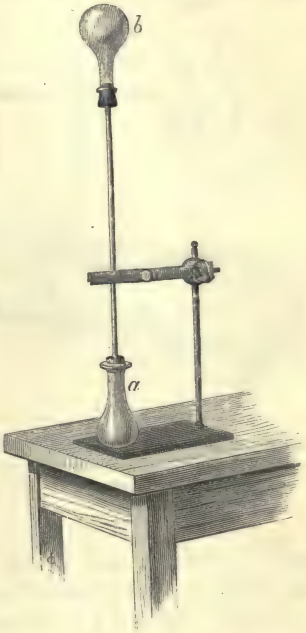
Diffusion of Hydrogen.—*a* Glass containing a coloured liquid; *b* jar closed at top by porous disc.

Hydrogen conducts sound very feebly, as it is easy to prove by agitating a small bell in a jar full of the gas, and then agitating it in a similar jar full of air.

12. It is the most difficult gas to keep, for its particles are so exceedingly light and mobile that they find their way out through any crack or imperfect joint more rapidly than any other particles. This important property is well illustrated by the processes of diffusion. If hydrogen be contained in a bell-jar, of which the mouth is closed by a porous disc of plaster of Paris, whilst the narrow opening dips into water, the gas escapes through the

porous disc so much more rapidly than the outer air can get in through it, that a partial vacuum is produced, and the water is rapidly sucked up into a bell-jar.

It might be supposed that a mixture of oxygen and hydrogen would gradually separate, the heavy oxygen falling to the bottom of the vessel, and the hydrogen rising to the top. Not only does no such separation of these gases by subsidence occur, but if a flask full of hydrogen be connected tightly, by means of a long narrow tube, with a second flask containing oxygen, and the tube placed in a vertical position, with the hydrogen in the upper flask, and the oxygen in the lower one, it is found that the two gradually but completely mingle, in opposition to the action of gravitation.

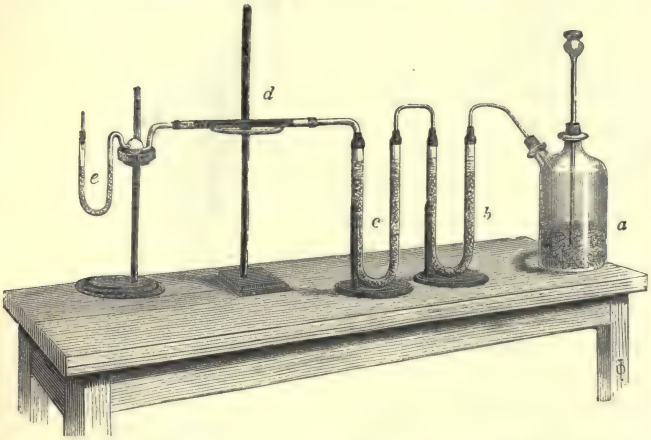


Apparatus to shew the Mixing of Gases by Diffusion.—*a* Flask full of oxygen; *b* flask full of hydrogen.

13. When a cold glass bottle is passed over a flame of hydrogen, it becomes coated with a dew-like film of moisture, which is formed by the combustion of the hydrogen, and at the same time the air loses some of its free oxygen. In order to prove that the combination of hydrogen and oxygen does form water, it is sufficient to heat some cupric oxide in a glass tube, and pass pure hydrogen slowly over it. The black oxide is speedily changed to red metallic copper, while the

oxygen carried away from it by the hydrogen forms water which can be collected.

The cupric oxide is obtained by burning metallic copper in the air. By taking due precautions the reduction of the oxide can be conducted in such a manner as to shew exactly the weight of oxygen taken from the cupric oxide, and the weight of water formed by the combination of this oxygen



Apparatus for the Reduction of Cupric Oxide by Hydrogen and for collecting the water.—*a* Bottle for evolving hydrogen; *b c* tubes containing materials for purifying and drying the gas; *d* tube containing cupric oxide; *e* tube for collecting the water.

with hydrogen; and it will then be found that every 8 grammes of oxygen taken from the copper form 9 grammes of water°. So that $\frac{1}{9}$ of the weight of water is due to hydrogen, and $\frac{8}{9}$ of its weight to oxygen.

14. Another way of arriving at the same result is to mix oxygen and hydrogen, in the proportion of one measure of oxygen and two measures of hydrogen, and to fire the

° $CuO + H^2 = Cu + H_2O$.

mixture by means of an electric spark in a strong glass vessel. After the explosion there will be no free hydrogen and no free oxygen left, nothing but water formed; whereas, if more than twice as great a volume of hydrogen be taken as of oxygen, the excess above the two volumes is left uncombined. By no expedient can the gases be got to combine directly with one another in any other proportion than that of one volume of oxygen to two volumes of hydrogen. Now we know that one volume of oxygen is sixteen times as heavy as one volume of hydrogen, and it follows that one volume of oxygen is eight times as heavy as the two volumes of hydrogen with which it combines to form water. The combustion of hydrogen in air is nothing else than a process of combination of hydrogen with the oxygen of the air, forming water, and every cubic centimetre of oxygen supplied by the air unites with two cubic centimetres of hydrogen.

A mixture of oxygen and hydrogen in these proportions is called **oxy-hydrogen gas**. It could be distinguished from steam by the following amongst other differences :—

Oxy-hydrogen Gas.	Steam.
1. Has a density of 6.	1. Has a density of 9.
2. Allows hydrogen to diffuse out more rapidly than oxygen.	2. Does not allow its hydrogen to diffuse out from its oxygen. They go together uniformly.
3. Explodes when sufficiently heated, forming steam.	3. Expands when heated, and returns on cooling to original state.
4. Cannot be condensed by cold and pressure to the liquid state.	4. Is easily condensed to water.
5. Allows its oxygen to be absorbed in the cold by phosphorus, pyrogallate, nitric oxide, &c.	5. Does not give its oxygen to any of these re-agents.
6. Is not absorbed by oil of vitriol, calcic chloride, or phosphoric acid, &c.	6. Is readily absorbed by any of these re-agents.

15. The combination of oxygen and hydrogen is accompanied by the evolution of intense heat; and a flame of

hydrogen, fed with oxygen in the proper proportion, in a suitable burner, is used for very strong heating effects. It is generally known by the name of the oxy-hydrogen burner. A piece of lime held in the flame becomes heated to so intense a white heat as to be valuable as a source of light.

One kilogramme of hydrogen gives off, on combining with the requisite weight of oxygen (8 kilogrammes), enough heat to warm 34,462 kilos. of water from 0°C to 1°C, or what is usually called 34,462 'degrees of heat' (not degrees of *temperature*).

16. Water is seldom found in nature in a state of purity. The peculiar qualities which belong to some waters are owing to the presence of foreign substances dissolved in them. Thus sea water contains from 3.5 to 4 per cent. of its weight of salts, which are left behind when the water itself is driven off by heat. These salts consist chiefly of sodium, potassium, magnesium, and calcium, combined partly as chlorides, partly as sulphates. Spring water presents the greatest varieties of composition, according to the nature of the soil through which it has percolated and the substances which it has taken up. Among mineral waters which are too strongly impregnated with foreign matter to be suitable for domestic use, and are confined to medical use, chalybeate waters are those which contain iron, hepatic waters contain sulphuretted hydrogen, whilst carbonic acid gas imparts to the waters which come in contact with it at high pressures the property of effervescing. Most kinds of spring water contain lime in solution, and possess the property of 'hardness' in consequence of the presence of this lime. The hardness of water is measured by 'degrees,' each degree representing 1 part by weight of carbonate of lime in 100,000 parts of water.

17. In order to remove mechanical admixtures with which

it may happen to be contaminated, water is filtered; but for the removal of dissolved solid matter the process of distillation is most convenient.

In chemical laboratories, where water is constantly used for operations in which the presence of lime, &c. would be perfectly inadmissible, spring water is usually distilled in an iron boiler, and condensed in a coil of copper tubing lined with tin. The spray which is usually carried up by the steam from the surface of the water, ought to be allowed to collect in an intermediate chamber before the pure steam passes on to the condenser.

At sea it is now becoming more and more customary to distil sea water for the use of the crew or passengers; but when first collected from the condenser, the water, however free from saline impurities, has a peculiar sickly flavour which renders it unfit for drinking. This flavour is completely removed by the customary practice of passing the water through a filter containing animal charcoal, and the water becomes charged at the same time with air, or 'aerated.'

For domestic use, water should be kept in wooden or iron cisterns. Zinc is also used sometimes with advantage; but the use of leaden cisterns is exceedingly dangerous, especially for keeping rain water, and ought under no circumstances to be permitted.

18. It was stated above that water is the sole product of the combination of oxygen and hydrogen, and by its decomposition the oxygen and hydrogen can be recovered again, in their original quantity and with unaltered properties. The easiest way to decompose water, for the preparation of free oxygen and hydrogen, is by the action of a strong galvanic current, on a mixture of water with hydric sulphate.

The wires which conduct the current should consist of platinum, and oxygen gas collects on the surface of one

of them, rapidly rising in bubbles through the liquid, while hydrogen rises from the surface of the other. A small loss of oxygen usually occurs, but the gases are nearly in the proportion of one volume of oxygen to two volumes of hydrogen if collected carefully.

This fact of the decomposition of water into two substances is an evidence of its containing two kinds of matter united together. Oxygen and hydrogen unite with one another to form water, and both of them can be recovered again from the water. Water is accordingly called a *compound* of oxygen and hydrogen. Oxygen has never been separated into different substances, and for this reason it is called an element. It undergoes various changes of property according to the conditions in which it is placed; but it resumes its original properties without difficulty when these conditions are reversed. All the more permanent changes which oxygen undergoes are due to processes of combination like those mentioned above, where it unites with other substances forming compounds from which it can be recovered again. Similar facts prove hydrogen to be an element. Chemical investigations have proved the existence of sixty-two elements, and every substance which has been examined is found to consist of one or more of these elements. A list of the elements is given in § 86, and appended to the name of each element is a symbol denoting a particular weight of that element, called its atomic weight.

When steam is passed through a tube intensely heated in a furnace, some of it is decomposed; but in order to collect any quantity of oxygen and hydrogen, it is necessary to separate them from contact with one another as soon as they are formed, as they would otherwise recombine.

For this purpose the tube through which the steam passes is made of a porous material (unglazed earthenware) and is

surrounded by a larger tube[p]. The hydrogen diffusing

[p] There are other compounds of oxygen analogous in their constitution to water, such as—

Nitrous oxide, N_2O.	Potash, K_2O.
Hypochlorous acid, Cl_2O.	Soda, Na_2O.
Silver oxide, Ag_2O.	

A second class of oxides is represented by the following bodies, viz.—

Hydric peroxide, H_2O^2. Silver peroxide, Ag_2O^2. Sodic peroxide, Na_2O^2.

A third class is illustrated by the following oxides, viz.—

Carbonic oxide, CO.	Cobaltous oxide, CoO.
Stannous oxide, SnO.	Nickelous oxide, NiO.
Platinous oxide, PtO.	Zinc oxide, ZnO.
Mercuric oxide, HgO.	Baryta, BaO.
Plumbic oxide, PbO.	Strontia, SrO.
Cupric oxide, CuO.	Lime, CaO.
Ferrous oxide, FeO.	Magnesia, MgO.
Manganous oxide, MnO.	

The fourth class is composed of oxides more acid in their properties, such as—

Carbonic acid, CO_2.	Platinic oxide, PtO_2.
Sulphurous acid, SO_2.	Plumbic peroxide, PbO_2.
Silicic acid or Silica } SiO_2.	Manganic peroxide, MnO_2.
Stannic oxide, SnO_2.	Baric peroxide, BaO_2.

The fifth class is represented by—

Nitrous acid, N_2O_3.	Bismuthic oxide, Bi_2O_3.
Chlorous acid, Cl_2O^3.	Ferric oxide, Fe^2O_3.
Phosphorous acid, P_2O_3.	Manganic oxide, Mn^2O_3.
Boracic acid, B_2O_3.	Chromic oxide, Cr^2O_3.
Arsenious acid, As_2O_3.	Alumina, Al^2O_3.
Antimonious acid, Sb_2O_3.	

The sixth class is less numerous: it contains—

Nitric peroxide, N^2O_4. Chloric peroxide, Cl_2O^4. Potassic peroxide, K_2O^4.

The seventh class consists of acids, such as—

Nitric acid, N_2O_5.	Antimonic acid, Sb_2O_5.
Phosphoric acid, P_2O_5.	Iodic acid, I_2O^5.
Arsenic acid, As_2O_5.	

The eighth class also consists of acids—

Sulphuric acid, SO_3.	Molybdic acid, MoO_3.
Selenic acid, SeO_3.	Tungstic acid, WO_3.
Telluric acid, TeO_3.	Chromic acid, CrO_3.

more rapidly than the oxygen, passes out through the porous tube into the external one.

19. Water combines with a great variety of substances, and the term **Hydrate** is used to designate a compound of water. Thus quick lime (calcic oxide) if merely moistened with water exhibits appearances which may be compared to combustion. Intense heat is evolved, and the light powder which is formed by the combination of the lime with the elements of water[q] is called calcic hydrate, or in common language, 'slaked lime.' The elements of water in this compound have properties different from those of uncombined water. They are solid, and not only do they not evaporate at the ordinary atmospheric temperature, and boil at 100°C, but it requires nearly a red heat for their expulsion from the compound. When phosphoric acid is moistened with water a similar combination takes place between the two bodies, forming a hydrate[r].

Soda also combines vigorously with water, forming a compound called sodic hydrate[s]. These hydrates are considered to belong to the general class of compounds called salts. The calcic and sodic hydrates have the power of imparting a blue colour to red litmus-paper, or a brown colour to turmeric.

The hydrate of phosphoric acid (called hydric phosphate) has an opposite action, for it restores the red colour of blue litmus or the yellow colour of brown turmeric; and it is shewn by these properties to be an acid salt. Its taste is sour or acid. Calcic hydrate and sodic hydrate are called basic substances (meaning anti-acid). If either of them be added to a solution of the acid phosphate, its acidity is gradually diminished and may be completely destroyed by the basic substance, whilst the base thus employed also loses

[q] $CaO + H_2O = CaH_2O_2$.

[r] $P_2O_5 + 3H_2O = 2H_3PO_4$.

[s] $Na_2O + H_2O = 2NaHO$.

its properties. The product thus obtained, if neither acid nor basic, is called *neutral*. There are many other oxides besides lime and soda which combine with water forming basic salts, and also many which like phosphoric acid form acid salts when brought in contact with water.

Oxides like lime and soda in this respect are called bases. Those like phosphoric acid are called acids. Water is a neutral oxide which does not neutralize the basic properties of bases nor the acidity of acids when it combines with either of them.

When salts are decomposed by the galvanic current, acids and bodies analogous to acids make their appearance at the positive pole, and are called electro-negative bodies; bases and substances analogous to bases appear at the negative pole, and are called electro-positive bodies.

In some compounds water is contained in a feebler state of combination than when combined with a strong base like lime, or with an acid. For instance, the crystals obtained by evaporating a solution of zinc sulphate contain water which can be driven off by heat, leaving the zinc sulphate anhydrous. This water is called water of crystallization, as it is less powerfully combined with the other materials than the water in hydrates. Water of crystallization possesses properties less different from those of free water than the properties of water contained in hydrates.

20. The effects of heat upon water are very remarkable, and deserve a careful study. If water be cooled to the temperature of 0°C, which is easily done by stirring it up with pieces of ice, and then allowed to absorb heat gradually in a warm room, it will be found that the water diminishes in volume while rising in temperature, and this goes on till the water has attained the temperature of 4°C. This is the temperature at which water is densest; for if heated above 4°C it expands with every degree of rise of temperature. Thus a

litre of water at 0°C becomes 0.99988 of a litre at 4°C, and at 9°C it has a volume somewhat greater than its original one, viz. 1.00005. Every degree further rise of temperature causes a greater proportional increase of volume: at 16°C the volume of the water is 1.00085; at 30°C it is 1.00406; at 50°C, 1.01177; at 70°C, 1.02225; at 100°C, 1.04299.

A litre measured off at 4°C expands to 1.043115 at 100°C. At 4°C the litre of water weighs 1000 grammes, called 1 kilogramme. At $16\frac{2}{3}$°C (62°F) a gallon of water weighs 70,000 grains, but at 4°C the gallon of water weighs 70007.2 grains.

When cooled to the temperature of 0°C, water can be made to give up heat, by contact with substances of a still lower temperature, but it does not for a time become colder by the process. It merely passes into the solid state, or, as we generally say, it freezes. The ice formed is however considerably bulkier than an equal weight of water: 94 grammes weight of pure ice occupy the same volume as 100 grammes of water at 4°C, thus the density of ice is 0.94.

Under favourable conditions the particles of ice arrange themselves at the moment of their formation in the form of regular six-sided prisms.

Appendix to Chapter II.

PROBLEMS.

11. What is the volume of 12 grammes of hydrogen at 15°C?

12. 100 cubic metres of hydrogen are supplied at 12°C. Wanted, the weight of a balloon which, when filled with the hydrogen, would press upwards with a weight of 20 grammes.

13. At what temperature has air the density which hydrogen possesses at the normal temperature (0°C)?

14. What loss of weight will 200 grammes of cupric oxide undergo when heated in contact with 2 grammes of hydrogen? What weight of water will be formed?

15. 4 litres of hydrogen at 0°C and 760 mm. are passed over an excess of red hot cupric oxide. What loss of weight does the oxide undergo? What volume of oxygen will be wanted to supply the place of that which was carried away by the hydrogen?

16. What volume of air is required for the oxidation of that quantity of metallic copper which is reduced from its oxide by 10 grammes of hydrogen?

17. 100 cubic centimetres of air are mixed with 50 cubic centimetres of hydrogen, and exploded by the electric spark. What is the volume of the residual mixture after explosion, supposing all the steam to be condensed?

18. What weight of potassic chlorate is required for the evolution of that quantity of oxygen which is needed for the combustion of 10 litres of hydrogen?

19. 20 kilogrammes of water have to be heated from 0° to 1°C by the combustion of hydrogen. What weight of hydrogen is needed for the purpose?

20. 200 litres of oxy-hydrogen gas are burned. What weight of water can be heated from 0°C to 1°C by the heat thus evolved?

21. An iceberg floating freely in sea water of density 1.027 is found to have a volume of 30,000 cubic metres above water. What is the total bulk of the iceberg?

22. A block of Wenham Lake ice weighs 280 kilogrammes. What is its volume?

CHAPTER III.

21. When water at 100°C is put over a fire, or otherwise exposed to heating action, it passes into steam, without getting hotter; so that a thermometer immersed in the boiling water continues to indicate the temperature of 100°C as long as the steam is being freely formed.

Any circumstances, however, which prevent the escape of steam enable water to undergo a rise of temperature when exposed to the action of heat. For instance, if the water be heated in a strong iron boiler, of which the outlet cock is closed, so that no steam can escape, the temperature rises above 100°C; and if the boiler be strong enough to resist the force with which the steam then presses against its sides, the water may be heated up to 200°C or 300°C, and even to still higher temperatures. If the experiment were performed in a boiler heated by a furnace and provided with a safety-valve, and if the valve were loaded more and more heavily, so as to subject the steam to the necessity of overcoming greater and greater pressure in order to make its way out, it would be found that when heated to 120°C, the water would give off steam almost capable of lifting a valve loaded 1.033 kilogrammes on the square centimetre ($14\frac{2}{3}$ lbs. on the square inch), and at a very slight elevation of temperature the valve would be lifted, and the water would boil at 120°C. By loading the valve further this ebullition could be stopped, and a load of about 3.1 kilos. on the square centimetre (44 lbs. on the square inch) would prevent the water from boiling till heated to about

144°C. In like manner it would be found, that at 170°C the tension of the vapour of water is about equal to a pressure of 7.23 kilos. on the square centimetre ($102\frac{2}{3}$ lbs. on the square inch).

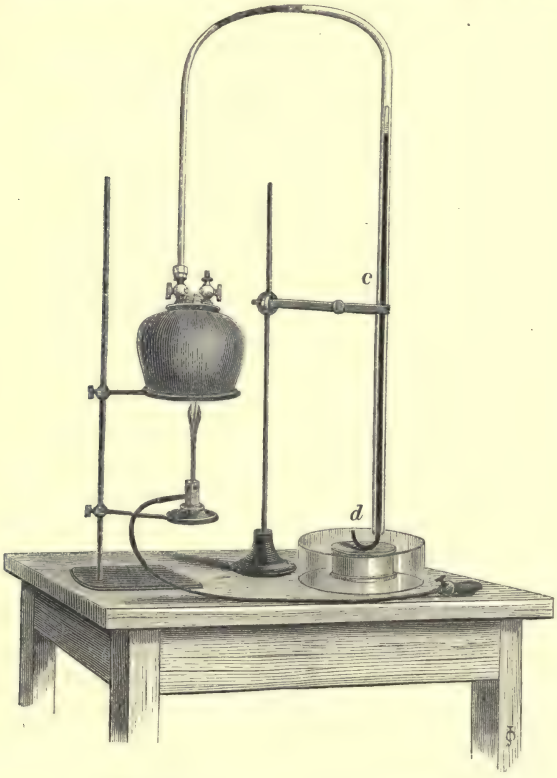
Now if the escape-pipe from the boiler be made to communicate with a closed condenser, from which all the air has been pumped out, so that steam on making its way from the boiler does not blow into the air, but into an empty space; it will be found that at the temperature of 100° the water in the boiler just boils when the valve is loaded 1.033 kilo. on the square centimetre ($14\frac{2}{3}$ lbs. on the square inch); and at 120°C it boils at a pressure of 2.066 kilos. ($29\frac{1}{3}$ lbs.); at 144°C it boils at 4.13 kilos. ($58\frac{2}{3}$ lbs.); and at 170°C it boils under a pressure of 8.26 kilos. ($117\frac{1}{3}$ lbs.). The removal of the atmospheric pressure by means of the air-pump is just made up for by an additional load on the valve of 1.033 kilo. on the square centimetre, or $14\frac{2}{3}$ lbs. on the square inch, or 2126.4 lbs. on the square foot, and we are thus led to infer that the boiling-point of water is the temperature at which the tension of its vapour is able to overcome the atmospheric pressure of — 1.033 kilo. on the square centimetre, or nearly 15 lbs. on the square inch.

A very simple experiment confirms the truth of this conclusion. Introduce a few drops of water into the vacuum of a barometer, as shewn in the annexed figure, and heat the instrument gradually to 100°C by steam. The mercury in the tube will gradually descend, and will stand at the same level inside the tube as outside it, when the water is heated to 100°C.

The tension of the vapour of water at temperatures below 100°C is measured by the depression of the column of mercury, produced by water heated to measured temperatures in the vacuum above it.

In the following table the results of observations of the

tension of steam, made at low temperatures by the aid of a barometer-tube, and made at high temperatures in a strong



Apparatus for heating water in a barometer.

boiler provided with a so-called pressure-gauge, are arranged in order.

The numbers given in the columns headed 'Tension in Millimetres' shew the height in millimetres of a column of mercury which could be supported by the steam.

By dividing any one of these numbers by 760 the amount of tension in atmospheres is obtained.

Tension (or Maximum Pressure) of Water-vapour between −32°C and +230°C (Regnault).

Temperature.	Tension in Millimetres.	Temperature.	Tension in Millimetres.	Temperature.	Tension in Millimetres.
°		°		°	
−32	0.320	55	117.478	145	3125.55
30	0.386	60	148.791	150	3581.23
25	0.605	65	186.945	155	4088.56
20	0.927	70	233.093	160	4651.62
15	1.400	75	288.517	165	5274.54
10	2.093	80	354.643	170	5961.66
5	3.113	85	433.041	175	6717.43
0	4 600	90	525.450	180	7546.39
+ 5	6.534	95	633.778	185	8453.23
10	9.165	100	760.000	190	9442.70
15	12.699	105	906.410	195	10519.63
20	17.391	110	1075.370	200	11688.96
25	23.550	115	1269 410	205	12955.66
30	31.548	120	1491.280	210	14324.80
35	41.827	125	1743.880	215	15801.33
40	54.906	130	2030.280	220	17390.56
45	71.391	135	2353.730	225	19097.04
50	91.982	140	2717.630	230	20926.40

22. When steam is heated by itself, without the presence of any liquid water, it is called **superheated steam.** But when there is water present, so that no excess of heat can accumulate in the steam above the quantity needed for its formation, under the pressure at which it exists, the **steam** is called **saturated**, meaning saturated with water. And when steam is mixed with small drops of liquid water (visible as fog) it is called **wet steam.** When saturated steam is heated for a few degrees above the temperature at which it was formed, it expands more than oxygen or hydrogen for each degree of temperature; but at still higher temperatures this anomaly does not exist, and steam then has the

co-efficient of expansion $\frac{1}{273}$. It follows from this that dry saturated steam at 100°C heated to higher temperatures in a closed vessel of sufficient strength, would increase a little more than oxygen or hydrogen in pressure for each degree rise of temperature near the point of saturation.

23. When, however, steam and water together are heated in a closed vessel, every degree rise of temperature causes the evaporation of some additional water into the limited space occupied by the steam, and consequently an increase of the density of the steam. In order to calculate approximately the **density of saturated steam** at any given temperature, it is necessary to ascertain by reference to the table what maximum pressure corresponds to the given temperature; and starting from the known density of steam at the normal temperature and pressure, to reckon its density at the given pressure by assuming it to behave like oxygen, i. e. to increase in density proportionally to the increase of pressure; then using the ordinary co-efficient of expansion ($\frac{1}{273}$), to compute how much the density calculated above would be reduced by heating the vapour from the normal temperature to that at which it has to be calculated.

24. The normal **density of steam** is best recollected in relation to that of hydrogen; for when two volumes of hydrogen weighing 2 grammes are combined with one volume of oxygen weighing 16 grammes, the 18 grammes of steam occupy just two volumes, so that each volume of steam weighs 9 grammes, and steam is therefore exactly nine times as heavy as hydrogen. The proportions by volume in which oxygen and hydrogen combine may be represented graphically.

Let a square figure be drawn of convenient size to represent one side of a cube of 11.2 litres capacity. This square figure represents a 'volume,' and it may be marked by the symbol and weight of any gaseous volume which has to be

represented. Thus $\boxed{H=1}$ denotes a volume of hydrogen weighing 1 gramme; $\boxed{O=16}$ denotes a volume of oxygen weighing 16 grammes, &c.

The combination of hydrogen with oxygen is represented by the diagram

$$\boxed{H=1} \quad \boxed{H=1} + \boxed{O=16} = \boxed{\frac{H^2O}{2}=9} \quad \boxed{\frac{H_2O}{2}=9}$$

which tells us that two volumes of hydrogen each weighing 1 gramme unite with one volume of oxygen weighing 16 grammes to form two volumes of steam each weighing 9 grammes.

If it were required to calculate the density of saturated steam at 150°, we should find by reference to the table that the tension corresponding to 150°C is about $4\frac{2}{3}$ atmospheres, or 4.71 kilogrammes on the square centimetre ($4\frac{2}{3}$ times $14\frac{2}{3}$ lbs. on the square inch). The increase from the normal atmospheric pressure of 1.033 to 4.71 kilos. will increase the density in like proportion, raising it from 9 to about 42. But the rise of temperature from 0° to 150°C will diminish this density in the proportion of 154.97 to 100, i.e. from 42 to 27.1. So that 27.1 is the approximate density of saturated steam at 150°, according to calculation.

25. When water evaporates into air, it is generally stated that it evaporates as into a vacuum; but this statement requires explanation. Suppose that a litre-flask were taken full of air at the pressure of 760 millimetres, and at the

temperature of 15°C, and that water were allowed to evaporate into this air until it was saturated with moisture at the same temperature. It is quite true that the litre-flask would then contain the same weight of steam as if no air were there. This weight can be ascertained by a calculation perfectly similar to that shewn for the weight of one volume of steam at 150°C, and it will be found that at 15°C, and the corresponding pressure of 12.7 millimetres, the density of steam is 0.1425; so that 11.2 litres weigh 0.1425 gramme, and 1 litre of it weighs 0.0127 gramme. The air in the flask continues to exert its original pressure, equal to 760 millimetres of mercury, on the flask sides, and the pressure of the steam is added to that, making the whole pressure $760 + 12.7 = 772.7$ millimetres.

When, on the other hand, bubbles of air pass through water in an open vessel, the moist bubbles which are formed expand immediately to a greater volume than the dry air from which they were formed, by the addition of steam. The moist air is therefore at the same pressure as the original dry air, but has gained in volume as much as, if enclosed in a flask, it would have gained in pressure by taking up steam. Thus, if a litre of air at 15°C and 760 millimetres mercurial pressure bubbled through water at 15° in an open vessel, the moist bubbles formed would occupy a volume greater than the litre in the proportion of 747.3 and 760, viz. 1.0169 litre, while remaining at the same temperature.

The pressure exerted by a bubble of air is equal to that of the surrounding atmosphere upon it, and is therefore measured by the barometer. This barometric pressure we may call B, and the tension of the steam corresponding to the temperature of the experiment may be called T. Then the air in the moist bubbles has a pressure $B - T$, while the tension of the steam makes up the loss of pressure caused by the expansion of the air.

The **boiling-point of water** was described above as the temperature at which the tension of steam is equal to the atmospheric pressure, so that the slightest addition of heat to any part of the water causes it to form bubbles of steam, and to lift the atmosphere enough to make room for those bubbles. But when water evaporates into oxygen or hydrogen gas at constant pressure, and forms a mixture of greater volume than the original dry gas, there is truly a lifting of the atmosphere to make room for the steam thus formed, as much as if it were by itself and unmixed with the permanent gas. So that at temperatures below its boiling-point water does evaporate, and lift the atmosphere, if in sufficiently close contact with a permanent gas; but only to such an extent that its volume, calculated at atmospheric pressure, stands to the volume of the permanent gas in the same proportion as the tension of the steam stands to the barometric pressure.

Thus, at -10°C the tension of steam is equal to 2.093 millimetres of mercury. A litre of dry air at the barometric pressure of 760 millimetres, in contact with ice at -10°C, would cause the evaporation of $\frac{1000 \times 2.093}{760}$ cubic centimetres of steam.

26. When **aerated water** is gradually heated in a glass vessel it gives off small bubbles of air before actually beginning to boil; and it must be kept briskly boiling for several hours, and cooled in a vessel to which atmospheric air has no access, if wanted perfectly free from air. If then brought in contact with oxygen gas at 0°C, it would dissolve about 4 per cent. of its volume of that gas. At 10°C it dissolves only $3\frac{1}{4}$ per cent. of oxygen, and at 20°C about 2.8 per cent. This dissolved oxygen is driven out again, with its original properties, by prolonged boiling.

Hydrogen is rather less than half as soluble as oxygen at

0°C; for 100 volumes of water take up, according to Bunsen, 1.93 volume of hydrogen, but at 10° and 20° the same volume is dissolved. Whether the experiment is tried at the atmospheric pressure or at a higher pressure, water still dissolves these same volumes of the gases and weights proportional to the pressure. Hence it is that water saturated with oxygen under pressure effervesces as soon as the pressure is removed, and only retains in solution the quantity of gas corresponding to the lower pressure.

27. The **quantity of heat** which water requires in order to undergo a rise of temperature of one degree centigrade is used as a measure of the quantity of heat which other substances require for 1°C elevation of temperature, and the term 'one degree of heat' means that quantity which heats 1 kilogramme of water from 0°C to 1°C. A kilogramme of oxygen undergoes 1° rise of temperature by about $\frac{1}{5}$ of a degree of heat; that is, it needs only about enough heat to warm $\frac{1}{5}$ of a kilogramme of water from 0°C to 1°C. The number 0.2175 represents the exact quantity as determined by Regnault, and is usually referred to as the specific heat of oxygen. **Hydrogen** has the highest **specific heat** of all known substances, the co-efficient being 3.4046. It is convenient to represent the specific heat of these two gases by volume instead of by weight; and as 16 parts by weight of oxygen occupy the same volume as 1 part by weight of hydrogen, we have only to multiply by 16 the specific heat of oxygen, in order to get the quantity of heat absorbed by 16 kilos. of oxygen, which are equal in volume to 1 kilo. of hydrogen. Now $16 \times 0.2175 = 3.48$, which is nearly the same as the heat absorbed by an equal measure of hydrogen. **The specific heat of steam** is 0.4805, or rather less than half that of water. It is worthy of note that the oxygen and hydrogen contained in 9 kilos. of steam have, before combination, capacities for heat amounting together to 5.145,

whereas the specific heat of 9 kilos. of the combined gases is only 4.3245.

Ice has a specific heat of 0.504 if examined between 0°C and −20°C, but if examined for the whole range of temperature from 0°C to −70°C it has a mean specific heat of smaller amount, viz. 0.474.

A careful comparison of the specific heat of water at different temperatures has shewn that at high temperatures the specific heat is somewhat greater than at low temperatures, as will be seen by the following examples calculated from a general formula which agrees with the observations—

at 0°C sp. H=1.0000;	at 50°C sp. H=1.0042.
at 100°C sp. H=1.0130;	at 150°C sp. H=1.0262.
at 200°C sp. H=1.0440;	at 230°C sp. H=1.0568.

Oxygen has the same specific heat at high temperatures as at low temperatures, and the same assertion no doubt holds good with regard to hydrogen. Oxygen is also found to have the same specific heat when examined under great pressure as when examined at its ordinary pressure and density.

Appendix to Chapter III.

PROBLEMS.

23. Ascertain from the tables the tension of steam at the following temperatures, viz. 70°C, 120°C, 140°C, 180°C; and calculate the density corresponding to each of these temperatures.

24. What is the density of steam at 760 mm. pressure, superheated to 200°C?

25. A room contains 80 cubic metres of air, saturated with moisture at 12°C and 760 mm. pressure. What would be

the volume of the air by itself, at the same temperature and pressure, after removal of the moisture?

26. A glass globe of 10 litres capacity is full of dry air at 100°C and 760 mm. pressure. Water is forced into it as long as it evaporates, the temperature being kept at 100°. What will be the tension of the moist air?

27. A mixture of air and steam is wanted containing one volume steam to two volumes air; and in order to obtain such a mixture it is proposed to bubble air through water kept uniformly at a temperature such that its vapour has the tension necessary. What is the temperature to which the water must be heated?

28. A subterranean cavity contains 30 cubic metres of water, at the temperature of 10°C. Hydrogen gas is bubbling through this water, and escaping afterwards at a pressure equal to 7,600 mm. of mercury. What weight of hydrogen will be dissolved in the water when it is fully saturated?

29. How many 'degrees of heat' are required to raise the temperature of 4 cubic metres of oxygen from 0°C to 100°C? What increase of volume will the oxygen undergo?

30. What weight of hydrogen would you have to burn in order to evolve enough heat to raise the temperature of 100 kilos. of steam from 120°C to 200°C?

31. What quantity of heat is obtained by cooling 90 grammes of hydrogen from 300°C to 0°C?

CHAPTER IV.

28. The letter O is used to denote an atom of oxygen, and in like manner H denotes an atom of hydrogen, and the symbol attached to the name of each element in § 86 means an atom of that element. The juxtaposition of two symbols is used to denote combination of the respective atoms: but when two or more atoms of like kind are combined together it is customary to put after and below the symbol of the atom a number shewing how many such atoms are combined together. Thus CO means a compound of one atom of carbon with one atom of oxygen; O^2 means a compound of two atoms of oxygen; H_2O means a compound in which two atoms of hydrogen are bound together by means of an atom of oxygen.

The index is placed above the symbol when the atoms are united directly with one another, as H^2; but below the symbol when only combined indirectly.

29. Each cluster of atoms united together is called a molecule, and the formula for such a cluster is called a molecular formula.

When several molecules have to be denoted the formula of one such molecule is written after the appropriate number. Thus $2H_2O$ means two molecules of water.

Every molecular formula, like H_2O, denotes a weight of the compound equal to the sum of the weights of the atoms contained in it, so that H_2O means 18 parts by weight of water. The molecule of water occupies in the state of

vapour exactly two volumes, whereas the three atoms which go to make it occupy together three volumes while uncombined.

CO is in like manner the molecular formula of a compound called carbonic oxide, containing an atom of carbon weighing 12, united with an atom of oxygen weighing 16. 12 + 16 grammes, or 28 grammes, is its molecular weight taken in grammes; and 28 grammes of carbonic oxide measure exactly two volumes (2 × 11.19 litres at 0°C and 760 millimetres).

The molecule of carbonic oxide occupies therefore the same volume as the molecule of steam.

If two volumes of carbonic acid (CO_2) were measured out and then weighed, they would be found to weigh 44 grammes, the weight (in grammes) denoted by the molecular formula of the acid.

Two volumes of sulphurous acid (SO_2) weigh 64 grammes, and two volumes of sulphuric acid vapour (SO_3) weigh 80 grammes.

One more example may suffice for the present purpose: viz. nitrous oxide, N_2O. Two volumes of this gas weigh 44 grammes.

In all these cases, viz. H_2O, CO, CO_2, SO_2, SO_3, and N_2O, the weight of two volumes of the vapour is called the molecular weight of the respective compound. The molecular weight of every substance which can be made to evaporate without decomposition is defined in like manner as the weight of two volumes of the vapour or gas.

30. The sign + interposed between symbols denotes addition of the atoms or molecules which the symbols represent, and in the proportions by weight corresponding to those symbols. In like manner the sign — between two symbols denotes the removal from one another of the atoms or molecules in the proportions described. The sign = is

used to denote chemical changes. It denotes equality in weight, between the sum of the atoms of each kind on one side of it and the sum of the atoms of the same kind on the other side of it. Thus H + O denotes a mixture of 1 part by weight of hydrogen with 16 parts by weight of oxygen. $H^2 + O = H_2O$ means that 2 parts by weight of hydrogen, added to 16 parts by weight of oxygen, can be made to combine to form 18 parts by weight of water. $H_2O - O = H^2$ means that if 16 parts by weight of oxygen are taken away from 18 parts by weight of water, 2 parts by weight of hydrogen are formed.

Brackets are frequently used to facilitate the comparison of two formulae. Thus in comparing the formulae $(SO_4)Zn$ and $(SO_4)H_2$, the use of brackets inclosing those constituents which are common to the two salts, serves to mark the fact that the difference between them is that one has got H_2, two atoms of hydrogen, while the other has got Zn, one atom of zinc. When several symbols are inclosed by brackets, and a number put after the group, the whole group is multiplied by that number.

31. Hydric Peroxide (H_2O^2). Oxygen and hydrogen do not unite directly in any other proportion than that in which they form water, but by indirect means a molecule of water can be made to combine with an atom of oxygen, forming hydric peroxide. For the preparation of this remarkable compound, baric peroxide (BaO^2) should be ground to a fine powder under water, and left for some time in contact with the water. A combination takes place forming a hydrated peroxide (BaH_2O_3). When this hydrate is dissolved in dilute hydric chloride, baric chloride is formed together with hydric peroxide—

$$BaH_2O_3 + 2(HCl) = Cl_2Ba + H_2O^2 + H_2O.$$

The baric chloride can be removed from the solution by carefully dropping into it a solution of argentic sulphate as

long as it continues to form a precipitate. The two soluble salts exchange metals, forming baric sulphate and argentic chloride, both of which are insoluble—

$$Ba\,Cl_2 + Ag_2\,S\,O_4 = 2\,(Ag\,Cl) + Ba\,S\,O_4;$$

and they settle at the bottom of the liquid, if it be allowed to stand; so that the solution of hydric peroxide can be poured off clear. In order to get rid of the greater part of the water which is mixed with the peroxide, the liquid is put into an open porcelain dish, under a glass bell-jar fitted on to the plate of an air-pump. A vessel containing strong oil of vitriol is also put under the bell-jar, and the air is then pumped out from it. In this vacuum the water evaporates rapidly, and is absorbed by the oil of vitriol, forming with it a compound far less volatile than water itself. In this manner a concentrated solution of peroxide is finally obtained of a specific gravity of 1.45. It bleaches litmus-paper.

32. This solution is rapidly decomposed by heat, giving off oxygen, and leaving water. It is also decomposed by various substances at the ordinary temperature. Thus, charcoal causes an immediate effervescence of oxygen in the solution, and finely-divided platinum, in the form called platinum-black, decomposes it still more rapidly. It is worthy of remark that the charcoal or platinum is found unchanged at the end of the decomposition, and although the peroxide gives up oxygen with the utmost readiness, it does not always allow other substances to combine with the oxygen which it is giving off. It frequently induces compounds containing oxygen to undergo a decomposition similar to its own, and to give off oxygen. Thus, potassic chromate, when dropped carefully into an acid solution containing hydric peroxide, is changed at first into a deep-blue body, and immediately afterwards turns green by giving off half the oxygen of the chromic acid with the oxygen which is escaping from the peroxide. Still more remarkable is the action of

the peroxide on the oxides of manganese: a mixture of manganic peroxide with hydric nitrate is deoxidized by hydric peroxide. Half of the oxygen which is given off comes from the hydric peroxide, whilst the other half comes from the manganic peroxide. The manganous oxide formed in this reaction is reconverted into peroxide by the action of hydric peroxide, in presence of an alkali or substance opposite to acids in its properties.

These remarkable phenomena have been investigated by Professor Brodie, and explained by him as due to the fact that oxygen from the one body combines with oxygen from the other, forming **free oxygen**, of which the molecule O^2 contains two atoms.

An *atom* of oxygen cannot exist by itself, and a couple of atoms is the smallest quantity of the element in the free state which can take part in any reaction.

The important rule stated in § 29 respecting compounds is thus extended to the element oxygen. Two volumes of free oxygen contain 32 grammes, and 32 is the molecular weight of oxygen.

In like manner hydrogen, nitrogen, chlorine, bromine, and iodine have the molecular formulae H^2, N^2, Cl^2, Br^2, and I^2, each molecule containing two atoms [u].

[u] Among hydrogen compounds (hydrides) there is less variety than among oxides. The simplest hydrates can be classified in four groups, viz.

First—	Third—
Hydric chloride, Cl H.	Ammonia, $N H_3$.
Hydric bromide, Br H.	Phosphuretted hydrogen, $P H_3$.
Hydric iodide, I H.	Arseniuretted hydrogen, $As H_3$.
Second—	Fourth —
Water, $O H_2$.	Marsh gas, $C H_4$.
Sulphuretted hydrogen, $S H_2$.	Siliciuretted hydrogen, $Si H_4$.
Seleniuretted, $Se H_2$.	

Another class is formed by Hydric peroxide, $O^2 H_2$, Hydric persulphide, $S^2 H_2$, Cuprous hydride, $Cu^2 H_2$.

Appendix to Chapter IV.

PROBLEM.

32. State in words the meaning of the following equations (ascertaining the signification of each elementary symbol from the table of atomic weights):—

$$Cl^2 + H_2O = ClH + ClHO;$$

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2(HCl);$$

$$NaCl + H_2SO_4 - HCl = HNaSO_4.$$

CHAPTER V.

33. Nitrogen[x], in the free state, is one of the most inert of gases, and is characterized by its inability to burn or to support combustion, and generally by its disinclination to combine.

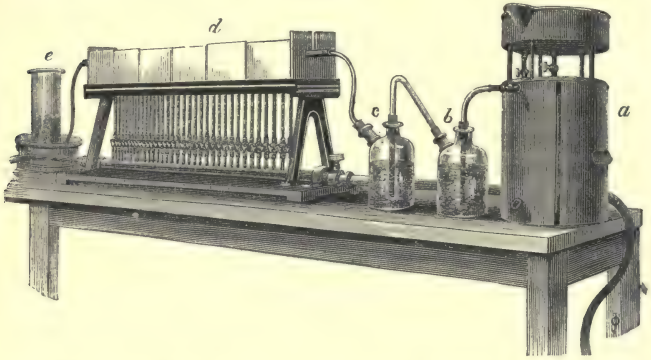
When combined with oxygen and hydrogen it forms a strongly acid compound belonging to the class of salts called nitrates. This acid nitrate is commonly called nitric acid[y]; and with less oxygen and more hydrogen it forms the compound called ammonic hydrate[z], which is a strongly basic, or in other words, a strongly anti-acid substance.

Nitrogen is the chief constituent of atmospheric air, and is best prepared from that source. A tube containing metallic copper, as obtained by the reduction of cupric oxide by hydrogen, is heated to redness, and a current of purified atmospheric air is then passed slowly into it at one end; pure nitrogen passes out at the other end. The purification of the air is effected by first passing it through a plug of cotton-wool in a tube, so as to strain off particles of dust, &c. which are contained in it, and then through a long tube or a bottle, containing solid potash, for the absorption of carbonic acid; and finally through a third long tube or bottle containing pumice moistened with strong sulphuric acid, for the absorption of water and ammonia. The oxygen is entirely absorbed

[x] Atomic symbol, N = 14. Molecular formulae, $N^2 = 2$ vols.
[y] NO_3H. [z] NH_5O.

by the metallic copper, and pure nitrogen can be collected as it escapes from the tube.

By arranging this experiment suitably, the relative weights of oxygen and nitrogen in air can be determined with great



Preparation of Nitrogen from Air.—*a* gas-holder containing air; *b* bottle containing potash; *c* bottle containing pumice and strong sulphuric acid; *d* furnace containing tube; *e* jar for collecting nitrogen.

accuracy. For this purpose a large glass globe, fitted with a good stop-cock, is exhausted by means of an air-pump, and then weighed. It is then connected with the end of the tube containing metallic copper, in such a way that all the nitrogen which passes through the tube shall go into the globe. The tube containing the copper must also be weighed before it is connected with the globe. As soon as the tube of copper is red hot, purified air is allowed to pass slowly through it. All the oxygen combines with the copper, while the nitrogen goes over to the exhausted globe. At the end of the experiment the globe is weighed again, and its increase of weight shews how much nitrogen there was in the air; the tube containing copper, now partially oxidized, is also weighed, and its increase of weight shews the quantity of oxygen in the air.

	by volume,	by weight,	
100 parts of air contain	20.9	23.1	of oxygen.
	79.1	76.9	of nitrogen.

Nitrogen is somewhat lighter than air; its density is 14, the density of air being 14.45.

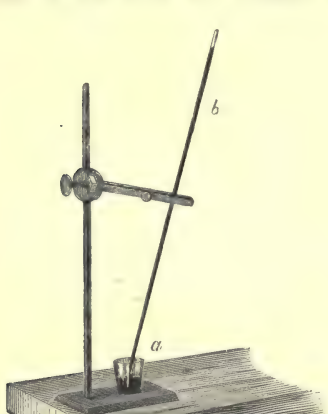
34. Nitrogen gas can also be obtained by heating ammonic nitrite. The salt is decomposed at temperatures below the boiling-point of water, forming nitrogen and water[a], and an aqueous solution of the salt accordingly gives off nitrogen gas with effervescence when heated. The most convenient way of obtaining the salt is to mix ammonic chloride and potassic nitrite in presence of water. The salts interchange bases forming potassic chloride and ammonic nitrite[b].

When heated at constant pressure nitrogen expands in the same proportion as oxygen and hydrogen for each degree rise of temperature, and the quantity of heat which one volume of it absorbs in order to undergo a rise of temperature of one degree is the same as the quantity absorbed by one volume of oxygen or of hydrogen. Nitrogen increases in density proportionally to the pressure to which it is subjected, and the greatest pressure and cold to which it has been subjected have failed to condense it to the liquid state.

35. The **weight** of the sea of air, or **atmosphere**, as it is generally called, is best investigated by means of a mercury **barometer.** A straight glass tube, nearly 1 metre long and closed at one end, is filled with mercury, care being taken to remove all the bubbles of air which at first adhere to its sides, by sweeping them away by means of one large bubble. The open end of the tube is then closed by the finger till dipped under mercury in a little cup. If the tube be then held vertically, the mercury in it will fall several inches

[a] $NO_2NH_4 = N^2 + 2\,H_2O$. [b] $KNO_2 + NH_4Cl = KCl + NO_2NH_4$.

below the top of the tube; but by inclining the tube the mercury can be made to fill the whole of it. In each position of the tube the column of mercury inside it will be the same height (measured vertically) above the mercury in the cup, if the tube be long enough to allow it to rise to that height. At the level of the sea and in the *normal* or ordinary state of the atmospheric - pressure, this height is 760 millimetres, or about 30 inches. When such a barometer is carried up to a height, so that there is a shorter column of air above it, the mercury falls; and in like manner the mercurial column rises to a greater height when the barometer is taken down any deep well or shaft.



Moveable Barometer to shew uniform height of mercurial column, with varying lengths. —*a* cup containing mercury; *b* moveable barometer tube.

When the barometer is put under a bell-jar, and a part of the air enclosed with it is gradually pumped out, so that the portion of air remaining in the bell-jar is of lesser and lesser density and corresponding pressure, the mercury falls in proportion to this diminution of pressure. Thus, if the mercury stood first at a height of 760 millimetres (30 inches) the removal of half the air from under the bell-jar would lower the pressure of the remainder to $\frac{1.033}{2}$ kilo. on the square centimetre ($\frac{14.7}{2}$ lbs. on the square inch), and the mercury would fall to 380 millimetres (15 inches). If $\frac{9}{10}$ of the air were

removed from the bell-jar, the mercury would stand at a height of only 76 millimetres (3 inches), the pressure of the remaining air on the surface of the mercury in the cup being 0.1033 on the square centimetre (1.47 lb. on the square inch).

A perfect **vacuum** would not support the mercury in the barometer at all; but even the best air-pumps are not perfect, they leave enough air to support half a millimetre, or sometimes less, height of mercury.

36. According to the results of Regnault's experiments, a **cubic metre of dry air**, measured at 0°C and 760 millimetres mercurial pressure, weighs 1.2932 kilogramme (or 100 cubic inches of dry air, measured at 0°C and 29.92 inches mercurial pressure, weigh 32.586 grains). In a cubic metre of air there are 10,000 columns of air of 1 metre high and of 1 square centimetre section, each of which weighs 0.00012932 of a kilogramme. In order to make up 1.033 kilo. (the actual weight of the air on each square centimetre) we should need 8,020 such columns of air 1 metre long, or a column of uniform density about 8,020 metres high. If the upper strata of the atmosphere were of this density as well as the lower strata, the height of the atmosphere would be 26,315 feet, or 5 miles all but 85 feet, above the level of the sea. But each stratum of air[c] has a density proportional to the superincumbent weight, and the higher strata have consequently a lesser density than the lower ones. If a bottle of 1 litre capacity were taken up to a mountain 5,486 metres high (about 18,000 feet), and there filled with air at 0°C, it would only take in half as great a weight as if filled at the level of the sea, viz. $\frac{1.2932}{2}$ gramme, because the stratum of air at that height has only half as great a pressure upon it as the lower air, and consequently only half as great

[c] At any fixed temperature.

a density. If the mouth of the vessel were closed by immersion in a vessel of mercury, and then brought down to the level of the sea while kept at the same temperature, it would be found that half a litre of mercury would be forced into the bottle by atmospheric pressure; so that the enclosed air would be at double as great a density as when collected on the top of the mountain. It is assumed that the level of the mercury inside the bottle is kept equal to the level outside, so as not to interfere with the atmospheric pressure on the contents of the bottle. It is computed that the air extends to a height of about 39,624 metres (130,000 feet), and that it is prevented by its own weight from expanding still further into the vacuum beyond it.

37. The **temperature of the atmosphere** is lower in elevated strata than near the surface of the earth, and this is easily accounted for by the fact that the air absorbs but a small part of the heat which is brought to it by the sun's rays, while the greater portion of the heat passes through the atmosphere, and heats the surface of the earth, or produces changes in its materials. The lower strata get heated in the day-time by contact with the hot ground, until their expansion renders them lighter than the upper strata, when a circulation immediately establishes itself. The evaporation of water in the lower atmospheric strata also causes a circulation; for the density of steam is less than $\frac{2}{3}$ that of air, and moist air is therefore lighter than dry air.

38. In the night-time, while the surface of the ground is receiving no heat from the sun, it is constantly giving off its heat, in the form of rays, more especially when the air above it is clear; and the lower strata of air are then cooled by contact with the cold earth. This cooling action often proceeds far enough to cause a condensation of moisture from the air, in the form of dew.

The **formation of dew** from the air is best studied with

the aid of a hygrometer. Daniell's hygrometer is a kind of cryophorous containing ether, and having one bulb blackened internally while the other bulb is covered by cambric. This cambric bulb is gradually cooled by dropping ether upon it, until moisture begins to be deposited from the air on the blackened bulb. A small thermometer contained in the ether of the blackened bulb is then read off, and at the same time a thermometer in the open air is read off. The difference between the two readings shews how much the air had to be cooled in order to begin to deposit moisture.

The temperature at which air begins to deposit moisture is called the **dew-point.** When the dew-point is many degrees below the temperature of the air, the air is capable of taking up more moisture, or, in other words, it is capable of drying a moist surface more rapidly than when the dew-point is but few degrees below the prevailing temperature. Thus it is that air containing a given quantity of moisture would be practically considered drier at 24°C than at 16°C.

If the dew-point of this air were at 16°C, or, in other words, if it contained as much steam as it could hold dissolved at 16°, it would have no drying action at that temperature, but a considerable one at 24°.

The quantity of steam dissolved in the air is too variable to admit of being estimated in any particular case by an average from many observations. In this country such an average would perhaps be about 1.5 per cent. of the volume of the air.

39. Two other essential constituents of air are carbonic acid and ammonia. 100 volumes of air usually contain about 0.04 of carbonic acid; but the proportion of carbonic acid is in many localities greater, and in ill-ventilated rooms is said to vary from 0.1 to 0.4, and even 0.7.

The **respiration of animals** not only removes oxygen from the air but replaces it by carbonic acid. Herbivorous

animals usually exhale carbonic acid, in volume equal to the oxygen which they absorb, but carnivorous animals appear to exhale a volume of carbonic acid smaller by 40 per cent. than that of the inhaled oxygen.

Dumas states that a man absorbs 220 to 245 cubic centimetres (from $13\frac{1}{2}$ to 15 cubic inches) of oxygen per minute, which amounts to a little more than 450 grammes (or about 1 lb.) per day. From 100 cubic centimetres of inhaled air, a quantity of oxygen varying from 4 to 6 cubic centimetres is usually removed at each inspiration. The average weight of water exhaled from the lungs per day is upwards of 500 grammes (or 7,716...grains), while that of carbonic acid is somewhat greater, viz. 550 grammes (or 8,487... grains).

To keep an inhabited room in a state of good **ventilation** for one person, 283 litres (10 cubic feet) of air should be removed every minute, and replaced by fresh air.

The proportion of ammonia in air is far smaller and also more variable than that of carbonic acid. Ten million volumes of air have been found to contain from 1.3 to 3.3 volumes of ammonia. Both carbonic acid and ammonia are given off and oxygen absorbed by decomposing vegetable and animal matter, and in some districts carbonic acid is evolved from vegetable matter underground, and when it comes in contact with water at high pressure, gives rise to effervescing springs. The processes of combustion of wood and coal which are now carried on for heating and mechanical purposes on a vast and increasing scale, constitute another drain of oxygen from the air and supply of carbonic acid.

40. The continual consumption of atmospheric oxygen in these various ways would gradually diminish its quantity, while replacing it by carbonic acid, were it not for the respiration of plants. Under the **influence of sunshine**, the leaves of plants absorb carbonic acid, and give off oxygen. At the

same time plants feed upon ammonia, and by their vital processes the elements of these substances and of water are elaborated into the varied compounds which we find in them —such as sugar, starch, wood, volatile oils, fatty oils, gluten, &c., &c. The processes by which these substances are formed might be called processes of unburning; for they are exactly the opposite processes to combustion. Not only do plants produce these combustible compounds while liberating oxygen, but they absorb from the sun's rays a vast quantity of heat, which they render latent, or store up in the form of wood and oils, &c., and of free oxygen.

The water of the sea, as well as of rivers and lakes, holds both oxygen and nitrogen in solution, and this air serves to support the respiration of fishes. It is richer in oxygen than atmospheric air, for 100 volumes of it contain upwards of 33 volumes of oxygen. This difference is owing to the fact that water dissolves nitrogen less freely than it does oxygen. At 0°C 100 volumes of water dissolve about 2 volumes of nitrogen; at 10°C only 1.6 volume; and at 20°C, 1.4: in each case about half as much as of oxygen. Marine plants absorb the carbonic acid, which is exhaled by fishes, and give off oxygen in its stead, thus helping to keep the composition of the air in water suitable for the respiration of the fishes.

Appendix to Chapter V.

PROBLEMS.

33. 50 cubic metres of nitrogen are in a gas-holder, and it is desired to add enough oxygen to make a mixture of the same composition as atmospheric air. How much potassic chlorate will be needed for the purpose?

34. An experimentalist fills with dry and pure atmospheric air, at the temperature of 10°C, a bottle of 1 litre capacity at

a height in the atmosphere such that a barometer stands at a height of 350 millimetres. What volume of oxygen and what volume of nitrogen will he have at the normal temperature and pressure?

35. Atmospheric air at the temperature of 15°C, and of which the dew-point is at 10°C, is passed over a moist surface of earth. What weight of water can each cubic metre of this air take up, supposing its temperature to remain at 15°C?

CHAPTER VI.

41. Nitrogen can be made to combine with oxygen, by mixing it with a large quantity of hydrogen, and burning the mixture. Electrical sparks passed through moist air also cause the formation of compounds of nitrogen, oxygen, and hydrogen, but both of these processes are too slow and costly for the preparation of large quantities of the compounds.

Five **compounds of nitrogen with oxygen** are known, viz. those represented by the formulae—

N_2O_5 Nitric acid.

N_2O_4 Nitric peroxide.

N_2O_3 Nitrous acid.

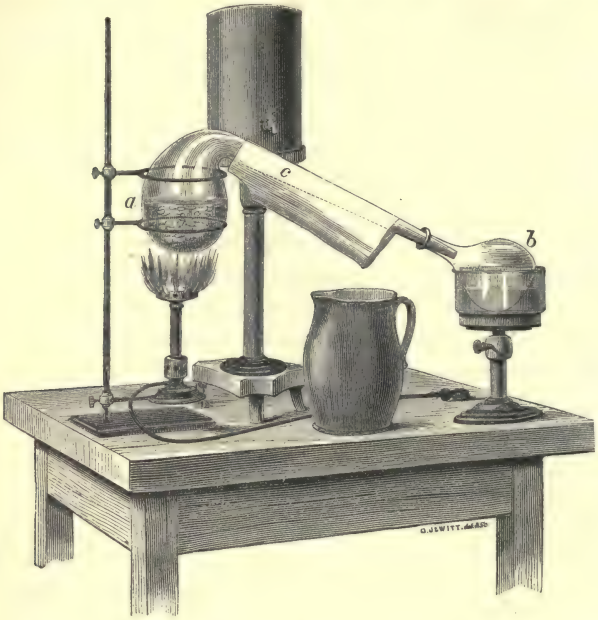
NO Nitric oxide.

N_2O Nitrous oxide, or laughing-gas.

Compounds of nitric acid are formed spontaneously by the contact of air with decomposing animal or vegetable matter containing nitrogen, in presence of bases. It is necessary that some base, such as lime, or potash, or soda, be present, to combine with the acid in proportion as it forms.

42. Potassic nitrate, or saltpetre, or nitre, as it is popularly termed, is generally used for preparing hydric nitrate on a small scale. The salt is mixed with an equal weight of hydric sulphate, and distilled in a retort until the contents of the retort fuse tranquilly, without giving off any more red fumes or condensable vapour. The yellow liquid which collects in the receiver has a density approaching to

1.5. It emits dense white fumes when brought in contact with moist air, by combining with the moisture of the air to form a compound less volatile than the original acid or



Preparation of Hydric Nitrate.—*a* Retort containing potassic nitrate and hydric sulphate; *b* receiver to collect distilled nitrate; *c* wet bibulous paper.

water. Even when mixed with large quantities of water the acid compound imparts a bright red colour to blue litmus-paper, and the original blue colour is restored by immersion in a solution of potash, or of soda, or lime, or any other substance possessing in a sufficiently strong degree the property of reversing the effect produced by an acid. When the acid is poured into a solution of potash, intense heat is

evolved, and if a good deal of water were not present with the substances, so great an elevation of temperature would be produced as to cause the mixture to boil, by the action of the opposite liquids on one another. By using dilute potash, and examining the liquid by litmus-paper after each addition, it is possible to destroy the power of blueing red litmus which the potash possessed, without imparting to the liquid the acid property of reddening blue litmus. The liquid is then termed neutral, and the compound of potassium which it contains is called potassic nitrate[d]. It is the very salt from which our acid was prepared by the action of sulphuric acid.

In order to explain the process by which hydric nitrate is prepared, it is best to compare the composition of the materials used in the process with the composition of the products finally obtained.

Oil of vitriol (hydric sulphate) is represented by the formula H_2SO_4; S being 32 parts by weight of sulphur, O being 16 parts by weight of oxygen, and accordingly O_4 being 64 parts by weight, and H_2 being 2 parts by weight of hydrogen. Potassic nitrate has the formula KNO_3, N being 14 parts by weight of nitrogen, and K 39 parts by weight of potassium. When the operation is complete, the fused mass in the retort, called hydro-potassic sulphate, has the composition $HKSO_4$; so that it is the same thing as hydric sulphate, from which 1 part by weight of hydrogen is taken away, and to which 39 parts by weight of potassium are added. The hydric nitrate collected in the receiver has a composition represented by the formula HNO_3, so that it is formed from potassic nitrate by removing K and putting in H.

The following equation

$$SO_4H_2+NO_3K=SO_4HK+NO_3H$$

[d] The process which takes place is represented by the equation
$HNO_3+KHO=KNO_3+H_2O$.

describes the process in its simplest form, as an interchange of K in nitre for H in oil of vitriol. It generally happens that the oil of vitriol contains a little water mixed with it, and this water goes over with the product. Some of the hydric nitrate, moreover, is decomposed by the heat, giving off oxygen-gas, and forming nitrous acid, a volatile compound of a yellowish red colour, which is generally seen in the distilling vessel, and which condenses in part with the acid in the receiver. By adding together the weight of sulphur, oxygen, and hydrogen, indicated by the formula of hydric sulphate, we have 98 as the weight of SO_4H_2, and in like manner 101 as the weight of NO_3K. The proportions represented by the formula are thus seen to be very nearly those of the experiment.

Hydric nitrate is an exceedingly acid salt; but the hydrogen contained in it acts the part of basic metal, and being endowed with feeble basic (or anti-acid) properties it does not neutralize the acidity which the compound owes to its oxygen. Hydric nitrate is so very acid a salt that it has very commonly been called 'nitric acid,' a name which properly belongs to the compound N_2O_5.

43. Hydric nitrate gives up a part of its oxygen with great facility to substances capable of combining with oxygen. When diluted with water its action is, however, less energetic than in the concentrated state, and by mixing it with oil of vitriol (a substance which tends to take water away from other compounds) the action of the nitrate is in most cases rendered even more violent than it is by itself.

Metallic copper thrown into dilute hydric nitrate of density 1.2 rapidly dissolves in it, while deep red fumes are given off in torrents; but if the experiment be performed in a vessel from which all atmospheric air has been previously removed, a colourless gas called nitric oxide is given off. The solution left at the end of the operation contains cupric nitrate.

The changes which take place in the process are represented by the equation

$$8\,HNO_3 + 3\,Cu = 2\,NO + 3\,Cu(NO_3)_2 + 4\,H_2O.$$

This reaction affords a very good means of detecting a nitrate. Strong hydric sulphate should be added to the liquid so as to form hydric nitrate from any other nitrate which may be present in the solution, and if much water be present the sulphate should be added in still greater quantity. The nitric oxide which comes off is easily recognised by the red fumes which it forms on coming in contact with atmospheric oxygen.

Nitrates are also detected by pouring a solution of ferrous sulphate into a mixture of equal volumes of strong oil of vitriol and the solution containing the nitrate. A brown colour shews itself immediately in the ferrous sulphate, if the quantity of nitrate present be considerable, or after some time if only a trace of the salt be present.

Metallic zinc dissolves in dilute nitrate even more readily than metallic copper, and a part of the nitrate is reduced to nitrous oxide (N_2O). By using the acid still more dilute, some of it is not only deprived of all its oxygen but combined with hydrogen, at the same time forming ammonia. This transformation is complete when the acid is reduced by metallic zinc in presence of metallic iron, in a great excess of caustic potash.

44. Nitric acid reacts on potash only in one proportion, and from this circumstance it is termed a **monobasic acid**. The process, when hydric nitrate combines with potassic hydrate, consists in a replacement of the hydrogen of the acid salt by potassium, in the proportion represented by the symbol of that element (K); and the hydrogen which leaves the acid takes the place of the metal, forming water according to the equation

$$HNO_3 + KHO = KNO_3 + H_2O.$$

The process is therefore an interchange of metals (H and K) between two salts, forming two new compounds which are nearly neutral. The weights of these substances are $NO_3H=63$, and $HKO=56$; and the equation states that hydric nitrate and potassic hydrate react on one another in the proportion of 63 parts of the acid salt to 56 of the basic salt. That they react on one another in no other proportion can be proved, by bringing the substances together in other proportions, on each side of this one—that is, with a greater proportion of base to the acid, so as to see if the acid can combine with more base; and then with more acid in proportion to the potash, in order to ascertain whether the base can combine with more acid, or the acid with less base. When an excess of potash is used the mixture is found to be alkaline to test-paper; and if a part of the water be carefully driven off from it by evaporation, the solution deposits crystals of nitre of the same composition as if no excess of potash had been present at their formation, and the excess of potash remains uncombined in the liquid from which the crystals have been deposited, or what is called the mother liquid. By using an excess of hydric nitrate to the potash, a perfectly similar result is obtained in an even more striking manner, for not only does the excess of acid remain uncombined with the potassic nitrate, but it can be distilled off from the salt and recovered unchanged.

It is thus proved that hydric nitrate and potassic hydrate react on one another in no other proportion than that represented by our equation.

We have here a case of vigorous action between two substances of very opposite properties giving off great heat and causing a disappearance of those properties; but it is proved to consist of both separations and combinations. If we write the formulae of the 'acid' and 'base' for convenience thus, $H(NO_3)$ and $K(HO)$, and the formulae of the

products similarly, K (NO_3) and H (HO), we see that H is separated from (NO_3) and K is separated from (HO), while K combines in the place of H, and H in the place of K. An atom is taken away from each of the compounds and another atom combines with each of the residues.

Processes of this kind are called **'double decompositions.'** Their general results present so much analogy with those which ensue in processes of apparently direct combination, such as we considered in § 4, that it is customary and proper to include them all under the general term chemical combination.

The forces which hold the substances together in the products are greater than those which held them together in the original compounds, so that weak forces are overcome in the separations by the exertion of the strong forces of combination[e].

[e] Nitrates may be classified similarly to hydrates in four chief families; the first being composed of such salts as—

Hydric nitrate, HNO_3.	Sodic nitrate, $NaNO_3$.
Potassic nitrate, KNO_3.	Argentic nitrate, $AgNO_3$.

The second class is composed of nitrates such as—

Stannous nitrate, $Sn(NO_3)_2$.	Cobaltous nitrate, $Co(NO_3)_2$.
Platinous nitrate, $Pt(NO_3)_2$.	Nickelous nitrate, $Ni(NO_3)_2$.
Mercuric nitrate, $Hg(NO_3)_2$.	Zinc nitrate, $Zn(NO_3)_2$.
Plumbic nitrate, $Pb(NO_3)_2$.	Baric nitrate, $Ba(NO_3)_2$.
Cupric nitrate, $Cu(NO_3)_2$.	Strontic nitrate, $Sr(NO_3)_2$.
Cadmic nitrate, $Cd(NO_3)_2$.	Calcic nitrate, $Ca(NO_3)_2$.
Ferrous nitrate, $Fe(NO_3)_2$.	Magnesic nitrate, $Mg(NO_3)_2$.
Manganous nitrate, $Mn(NO_3)_2$.	

The third class contains such nitrates as—Bismuth nitrate, $Bi(NO_3)_3$.

The fourth, salts like Platinic nitrate, $Pt(NO_3)_4$.

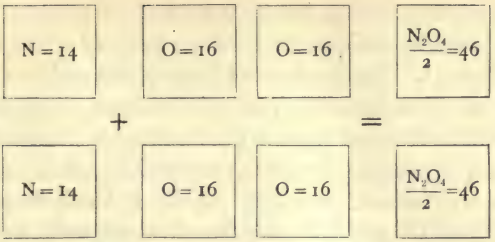
CHAPTER VII.

45. Nitric Acid (N_2O_5) has not been obtained by removal of water from the hydrogen salt. It is prepared by passing chlorine gas over argentic nitrate, and condensing the products in a receiver cooled to a very low temperature. It is a solid crystalline compound, possessing the above composition. When brought in contact with water it combines, with evolution of heat, to form hydric nitrate according to the equation $N_2O_5 + H_2O = 2NO_3H$. When kept in a closed tube it has been found to explode with violence, and without any external aid.

Nitric Peroxide (N_2O_4) is most conveniently obtained by heating plumbic nitrate in a stone-ware retort, and condensing in a cold receiver the red fumes which escape. The process consists in a breaking-up of the salt into plumbic oxide, which remains in the retort, and nitric peroxide and oxygen which pass off—

$$PbN_2O_6 = PbO + N_2O_4 + O.$$

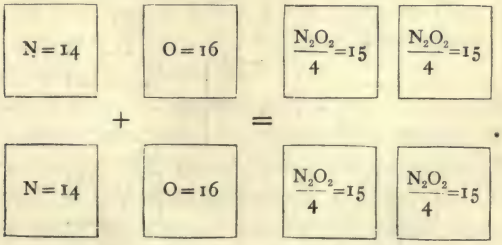
The peroxide is at the ordinary atmospheric temperature a yellowish red liquid, but when cooled a few degrees below 0°C it becomes colourless. In contact with water it is decomposed, forming hydric nitrate and a lower oxide of nitrogen. It does not appear to combine with bases. When evaporated by the aid of heat in the pure state its vapour has a density corresponding to $N_2O_4 = 4$ vols. But when evaporated at a lower temperature in presence of a permanent gas it approaches the normal density corresponding to $N_2O_4 = 2$ vols.



46. Hydric Nitrite (HNO_2) is a very unstable compound, and is but little known even in its saline derivatives. The red colour of hydric nitrate which has been exposed to the action of light is owing to the presence of nitrous acid. It is decomposed by water, forming hydric nitrate and nitric oxide. The nitrites have much resemblance to nitrates. Nitrous acid is easily obtained by heating starch with a large quantity of hydric nitrate of density 1.25.

Nitrous acid (N_2O_3) is formed by mixing nitric oxide (NO) with free oxygen, in the proportion of not more than one-fourth of its volume. The red vapour which is formed does not condense at 0°C, but if the vessel containing it be cooled to a temperature of about −20°C the acid condenses to a deep blue liquid.

47. Nitric Oxide[f] is most conveniently prepared by dissolving copper in nitric acid of density 1.2 to 1.3. Its theoretical molecule (N_2O_2)



[f] NO = 2 vols.

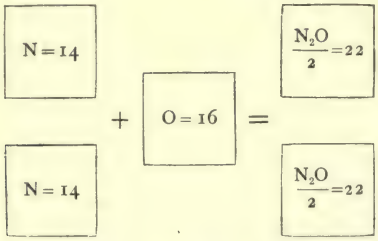
occupies four volumes, the same as that occupied by a mixture of nitrogen and oxygen in these quantities. Its density is therefore 15. The gas has not been condensed to a liquid, by the greatest pressure and cold hitherto applied to it. Nitric oxide does not support the combustion of some kinds of wood; but more powerful combustibles, such as phosphorus or charcoal, burn very rapidly if kindled and then plunged into the gas. It combines with sulphuric acid.

When two volumes of nitric oxide are mixed with not less than five volumes of hydrogen, and passed through a red-hot tube containing spongy metallic platinum, the mixture is transformed into ammonia and water.

48. Nitrous Oxide, or laughing-gas ($N_2O = 2$ vols.), is most readily prepared by gently heating ammonic nitrate. Water and nitrous oxide are the only products, and the decomposition takes place according to the equation

$$N_2O_3H_4 = N_2O + 2H_2O.$$

The gas dissolves in water at 0°C to the extent of 1.3 of its volume, and at 15°C water dissolves more than two-thirds of its volume. It is therefore customary to collect the gas by displacement of hot water in the pneumatic trough. It may also be collected by displacement of air, if led to the bottom of a jar full of air, as it is about half as heavy again as air. Its exact density is 22.



$$8NO - 5H = NH_3 + H_2O.$$

Nitrous oxide is a colourless gas, devoid of odour; but it produces when inhaled inebriating effects, which have gained for it the trivial name of laughing-gas. It supports the combustion of most substances with an intensity so nearly equal to that with which oxygen supports combustion that it might be mistaken for that gas, if carelessly examined. A kindled splint bursts into flame in nitrous oxide as in oxygen. Phosphorus burns with dazzling splendour in nitrous oxide, liberating nitrogen in volume equal to the original gas. This circumstance affords a distinction between nitrous oxide and oxygen. Nitric oxide does not produce red fumes when mixed with nitrous oxide. Potassic pyrogallate does not absorb nitrous oxide as it does oxygen.

Nitrous oxide can be condensed into a liquid at the temperature of 0°C by a pressure of about 36 atmospheres, and the **liquid nitrous oxide** is one of the most powerful cooling agents known. When some of the liquid is removed from the vessel in which it was formed by pressure, and brought out into an open vessel, it boils with great violence, and the portion which evaporates absorbs so much heat, that the remaining liquid is cooled to a temperature of about -88°C, at which it boils under the common atmospheric pressure.

A still lower temperature is obtained by placing this liquid in a vacuum, maintained by a powerful air-pump, and the accelerated evaporation which takes place at that greatly reduced pressure, serves to freeze some of the nitrous oxide into a transparent solid like ice.

The co-efficient of expansion of nitrous oxide gas is very slightly greater than that of oxygen. The specific heat of the gas is .2238. The specific heat of a mixture of oxygen and nitrogen in the same proportions is .2284.

It has lately been found that nitrous oxide forms salts corresponding to the nitrates and nitrites—

HNO_3 Nitrate.
HNO_2 Nitrite.
HNO Hyponitrite.

The sodium salt was formed by the action of sodium-amalgam upon sodic nitrate, the nitrite being first formed, and subsequently reduced to hyponitrite with the formation of nitrous oxide. The silver salt NOAg is a yellow pulverulent precipitate, insoluble in water and in hydric acetate, but soluble in dilute hydric nitrate and in ammonia.

Appendix to Chapters VI and VII.

PROBLEMS.

36. What weight of hydric nitrate HNO_3 ought to be obtained from 1 kilogramme of sodic nitrate $NaNO_3$, supposing none of the product to be decomposed?

37. How much hydric sulphate is required for the decomposition of 500 grammes of potassic nitrate, according to the equation

$$H_2SO_4 + 2KNO_3 = K_2SO_4 + 2HNO_3?$$

38. 10 grammes of nitric oxide are required; what weight of the materials would you require for their formation?

39. What weight of water is formed by the reaction of 200 grammes of hydric nitrate upon potassic hydrate, according to the equation

$$HNO_3 + HKO = KNO_3 + H_2O?$$

40. 300 grammes of pure hydric nitrate are mixed with 800 grammes of potassic hydrate. How much more of the nitrate must be added in order to render the mixture neutral?

41. What weight of oxygen is liberated by the gradual action of heat on 300 grammes of plumbic nitrate?

42. What volume of nitric oxide is required for the com-

bustion of 10 cubic centimetres of hydrogen? and what will be the volume of the nitrogen liberated?

43. What volume of oxygen is needed for the conversion of 10 grammes of nitric oxide (in presence of water) into hydric nitrate?

44. What weight of nitrous oxide is obtained from a kilogramme of ammonic nitrate? and what is the volume of the gas at the normal temperature and pressure?

45. What volumes of the free gases would you obtain by the decomposition of a litre of nitrous oxide?

46. What volume of hydrogen could be burnt by 10 grammes of nitrous oxide?

CHAPTER VIII.

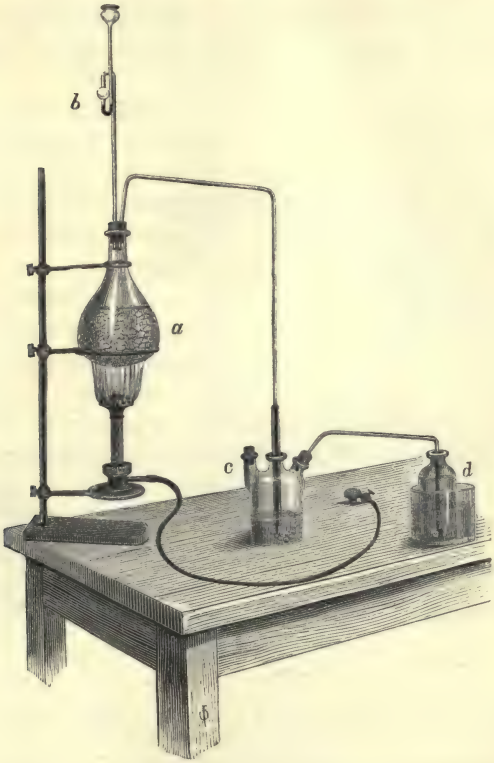
49. Ammonia (NH_3) is a minor constituent of the atmosphere, and is given off by putrifying animal and vegetable substances containing nitrogen. It is also one of the products of the decomposition of coals by heat, and is collected in large quantities at gas-works. It is usually obtained by the action of lime on sal-ammoniac. The lime should be previously slaked, that is, combined with water, and the light powder thus obtained should be mixed with about two-thirds of its weight of finely-powdered sal-ammoniac, and the mixture heated in a flask similar to that used for evolving oxygen, fitted however with a wash-bottle to wash the gas. Sal-ammoniac is a compound of ammonia with hydric chloride, and the lime takes the chloride from it, whilst ammonia is liberated, together with the water from the lime.

The reaction is thus described by an equation:

$$2NH_4Cl + CaH_2O_2 = 2NH_3 + CaCl_2 + 2H_2O.$$

The ammonia gas is usually led into water, and the solution thus obtained goes commonly by the name of ammonia. The gas itself can be collected by displacement of mercury, or for some purposes it might be collected like hydrogen, by displacement of air, by leading it up to the top of a bottle suspended mouth downwards. Its density is 8.5. If required free from moisture it should be passed through a tube containing powdered potassic hydrate. Ammonia is remarkable for its pungent smell, and it exerts so powerful a corrosive action on moist animal tissues that the most serious

consequences might arise from inhaling any considerable quantity of it. A piece of red litmus-paper immediately



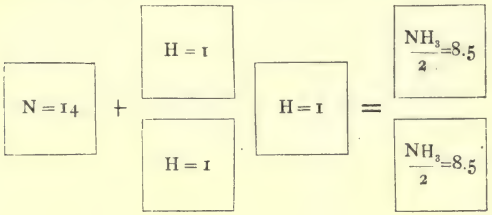
Preparation of Ammonia Solution.—*a* Flask containing sal-ammoniac and lime; *b* safety tube; *c* wash-bottle; *d* bottle containing distilled water to be saturated.

turns blue by contact with ammonia, and nitric acid is neutralized by ammonia as effectually as by potash itself, so that ammonia is justly entitled to the name which is frequently

given to it, of volatile alkali. When a glass rod, moistened by hydric nitrate of such strength as not to fume in the air, is brought in contact with ammonia, dense white fumes are formed, owing to the formation of solid ammonic nitrate in the air, by contact of the vapour of the nitrate with the volatile alkali.

Ammonia burns with the greatest difficulty; but when mixed with oxygen it can be exploded, and if sufficient oxygen be present ammonic nitrate is formed by the explosion. A gradual oxidation of ammonia, forming ammonic nitrite, takes place at the common atmospheric temperature, in presence of finely-divided metallic copper.

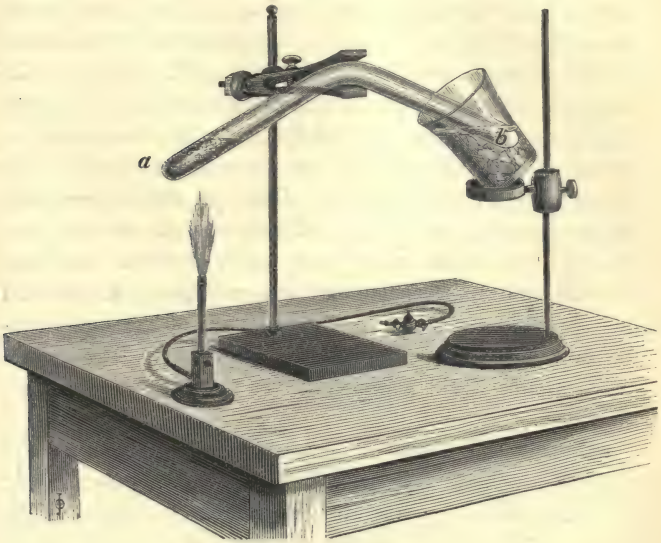
When passed through a red-hot tube ammonia is decomposed, and the same result can be obtained by passing a succession of electric sparks through ammonia gas confined in a glass tube over mercury. The mixture of nitrogen and hydrogen formed by the **decomposition of ammonia** occupies exactly double the volume of the compound of the two gases.



The expansion of ammonia gas by heat takes place very nearly in the same proportion as that of oxygen, hydrogen, or nitrogen, the coefficient of expansion of ammonia being slightly greater than that of the permanent gases. The specific heat of ammonia is .5083, which is considerably less than that of the nitrogen and hydrogen contained in it. The specific heat of a mixture of hydrogen and nitrogen in the

proportions in which these gases are contained in ammonia is .802.

50. Ammonia can be condensed to a liquid of about 0.76 density, by passing the gas slowly into a tube cooled by a powerful frigorific mixture below the temperature of −38.5, at which **liquid ammonia** boils at the ordinary



Preparation of Liquid Ammonia.—*a* Heated end of tube containing compound of silver-chloride and ammonia; *b* cooled end of tube where liquid ammonia collects.

atmospheric pressure. At the temperature of 10°C it requires a pressure of about 6 atmospheres for its liquefaction. The easiest way to prepare this liquid on a small scale is to saturate some dry silver chloride with ammonia gas, and to put the compound into a strong glass tube, sealed up at one end

and bent in the middle at an angle of about 120°. The tube is then sealed up at the other end, by the aid of a blow-pipe flame, and when cold is ready for use. If the empty end of the tube be surrounded by ice, whilst the end containing the compound of ammonia and argentic chloride is heated by means of a water bath, the ammonia is gradually expelled from the compound, and is confined by the narrow dimensions of the tube at so great a pressure, that a considerable proportion of it condenses in the cold end of the tube. Liquid ammonia solidifies at about −90°C. A solution of ammonia in water, saturated with the gas at a low temperature, gives off a large part of the gas when heated, and a strong solution of ammonia can therefore be used for the preparation of liquid ammonia. The operation is performed in iron vessels from which all atmospheric air has been removed, and if the water from which ammonia has been expelled by heat be cooled again, it condenses the ammonia gas above it, and causes an evaporation of the liquid ammonia which has been previously condensed. The evaporation of this liquid ammonia serves to freeze water outside the vessel.

51. Ammonia dissolves in water with great rapidity, and gives off a considerable quantity of heat in the process. At 0°C water takes up more than 1000 times its volume of the gas, at 15°C upwards of 700 volumes, and at 24°C nearly 600. The solutions smell strongly of ammonia, and when saturated give off a part of the gas with extreme readiness. Their density is less than that of water, and the strongest solutions have the smallest density. Quantitative determinations have been made of the proportion of ammonia and water in solutions of various densities, and the results of these determinations are recorded in tables, which should be consulted whenever it is wanted to know the strength of a solution of which the density has been

ascertained. One of these tables will be found at the end of the volume.

Ammonia, when **dissolved in water,** must be considered to be in combination with one molecule of water, in the form of the compound NH_5O. In the reaction of aqueous ammonia on hydric nitrate, forming ammonic nitrate and water, there is a process perfectly similar to that which occurs when aqueous potash reacts upon the salt; but in order to see the resemblance, we must arrange the elements of the compound of ammonia and water, so as to shew its analogy with the potassic hydrate (K) H O. For that purpose we can write it (NH_4) H O, so that the group of elements NH_4 is contained in the aqueous ammonia instead of the element K in the potassic hydrate. We have then to represent the reaction of the nitrate by the following equation, viz.

$$HNO_3+(NH_4)HO=(NH_4)NO_3+HHO;$$

just like

$$HNO_3+(K)HO=(K)NO_3+HHO.$$

The action of solution of ammonia on nitrates containing other weak bases is analogous to the action of potash upon them. Thus, potash precipitates plumbic hydrate from a solution of plumbic nitrate, and ammonia effects a similar decomposition, though rather less effectually:

$$Pb(NO_3)_2+2KHO=2KNO_3+Pb(HO)_2.$$

$$Pb(NO_3)_2+2(NH_4)HO=2NH_4NO_3+Pb(HO)_2.$$

The alkalies and alkaline earths are stronger bases than ammonia, and are not separated from acids by it.

52. It will be seen by the further study of ammonia that it reacts on nearly all acid hydrogen salts in a similar manner to potash, and that NH_4 plays the same part in the salts of ammonia which K plays in the salts of potassium. In fact this group of elements (NH_4) is in its compounds like the

metal potassium. For these reasons it is found convenient to give to this group of elements a name bearing some resemblance to the names of metals, and the object is attained by calling it **ammonium**[h]. Ammonium is at present only known in compounds, as it is always decomposed into ammonia and hydrogen as soon as it is turned out of combination. The nearest approach to free ammonium is a compound of mercury with it, a substance in which the metal mercury is united with the compound metal ammonium so feebly that the properties of the constituents are less altered than in firmer compounds. The compound is easily obtained by putting sodium-amalgam into a strong solution of sal-ammoniac. The sodium rapidly dissolves, taking the chlorine from the ammonium, while the ammonium combines with the mercury. A soft buttery mass is thus obtained, occupying an enormous volume compared with that of the original mercury—

$$Na\,Hg_n + NH_4\,Cl = NH_4\,Hg_n + Na\,Cl.$$

The ammonium amalgam very rapidly decomposes when removed from the liquid, and gives off a mixture of two volumes of ammonia to one volume of hydrogen.

53. Ammonic Nitrate (empirical formula $N_2O_3H_4$, rational formula NO_3NH_4) is easily prepared by dissolving ammonic carbonate in hydric nitrate, and evaporating the solution till it crystallizes. The salt is then deposited in the form of needle-shaped crystals, which can be dried on

[h] AMMONIUM COMPOUNDS—

Ammonic chloride, NH_4Cl.
„ cyanide, NH_4CN.
„ nitrate, NH_4NO_3.
„ hydrate, NH_4HO.
„ sulphate, $(NH_4)_2SO_4$.
„ sulphite, $(NH_4)_2SO_3$.
„ oxalate, $(NH_4)_2C_2O_4$.
„ carbonate, $(NH_4)_2CO_3$.
„ phosphate, $(NH_4)_3PO_4$.

POTASSIUM COMPOUNDS—

Potassic chloride, KCl.
„ cyanide, KCN.
„ nitrate, KNO_3.
„ hydrate, KHO.
„ sulphate, K_2SO_4.
„ sulphite, K_2SO_3.
„ oxalate, $K_2C_2O_4$.
„ carbonate, K_2CO_3.
„ phosphate, K_3PO_4.

bibulous paper. Ammonic nitrate dissolves in water very rapidly, and in very large quantity. Its liquefaction absorbs a considerable quantity of heat, which is evolved again when the salt crystallizes out from its solution. The salt is frequently used for producing a low temperature for the formation of ice, and is recovered again after use by evaporation of its solution. When thrown on to red-hot coals the salt explodes, but when heated gradually by means of a lamp it decomposes entirely into nitrous oxide and water.

Ammonic nitrite ($N_2H_4O_2$ or $NO_2(NH_4)$) is a very unstable salt. It can be obtained by decomposing plumbic nitrite by ammonic sulphate. The solution decomposes when heated, giving off nitrogen gas.

A solution of ammonia precipitates a solution of cupric sulphate, but when added in greater quantity it dissolves the precipitate, forming a deep azure-blue solution. Ammonic chloride forms with platinic chloride a compound very slightly soluble in water, and insoluble in alcohol. It possesses the composition $Pt(NH_4)_2Cl_6$. The most delicate **test for ammonia** is Nessler's test, viz. potassic iodide saturated with mercuric iodide. When mixed with an excess of potash, this solution gives a reddish yellow colour with a liquid containing the least trace of ammonia, and gives a precipitate with very small quantities of ammonia.

Oxyammonia or **Hydroxylia** (NH_3O). This body has been obtained by passing a current of nitric oxide through a solution in which hydrogen is being evolved, as through a mixture of tin and hydric chloride. The reaction appears to be essentially—

$$N^2O_2 + 3H_2 = 2NH_3O.$$

The basic compound combines with hydric chloride, and the hydrochlorate can be obtained in crystals, after the precipitation of the tin by sulphuretted hydrogen, mixed with

sal-ammoniac, formed at the same time. It is separated from the latter by treating the mixture with boiling alcohol, which dissolves only the hydro-chlorate of hydroxylia.

It is also produced in the reduction of ethylic nitrate by nascent hydrogen. It forms salts like ammonia by direct addition; thus the formula of the hydrochlorate is $NH_3O.HCl$; and that of the oxalate $(NH_3O)_2C^2H_2O_4$.

Appendix to Chapter VIII.

PROBLEMS.

47. What will be the dimensions of a flask capable of containing 20 grammes of ammonia gas, at 12°C and 730 mm. pressure?

48. What weight of sal-ammoniac must be taken to obtain 1 kilogramme of ammonia?

49. What volume of nitrogen is obtained by the combustion of 10 cubic centimetres of ammonia?

50. What volume of nitrogen will be evolved by the action of nitrous acid on 10 grammes of ammonia?

51. 100 grammes of nitre (KNO_3) are distilled with hydric sulphate. What weight of ammonia will be required to neutralize the distillate? and what will be the weight of the nitrate formed?

52. 3 grammes of nitric oxide are mixed with an excess of hydrogen and passed over moderately heated platinum sponge. What weight of ammonia is formed?

53. 2.14 grammes of ammonic chloride (NH_4Cl) were obtained by the action of metallic zinc in presence of iron on a mixture of a nitrate with potash solution. What weight of nitric acid (N_2O_5) was required for its formation?

54. A weighed quantity of an organic substance containing nitrogen was heated with soda-lime, and the ammonia was passed into hydric chloride and combined with platinic chloride. 3.428 grammes of the double chloride were thus obtained. How much nitrogen is contained in this?

CHAPTER IX.

54. Carbon occurs as diamond, plumbago, charcoal, &c. It is remarkable for the great difference between the properties which it possesses in these different substances, differences which are not owing to the presence of any foreign substance in any of these varieties of carbon, but which belong to the carbon itself. Diamonds have a density of about 3.55, whilst plumbago has only a density of about 2.2. Diamond is the hardest known substance, whereas plumbago is so soft that even paper rubs off particles from it. Diamond is transparent, plumbago is opaque. Diamond is a very bad conductor of electricity, and usually ranks among non-conductors. Plumbago, on the contrary, conducts well, and equals some metals in this respect. Diamond crystallizes in octohedral forms, or in forms nearly related to them, plumbago crystallizes in six-sided plates. The specific heat of diamond is .14687, while that of plumbago is .2008, and that of charcoal .2415. These substances are so entirely different in their properties that they could not be classed together at all, were it not for the fact that both of them can be made to combine with oxygen, and, once combined, retain no traces of the original differences between them, for carbonic acid made from diamonds is identical with carbonic acid made from plumbago. At a very high temperature, such as that obtained by discharging a powerful galvanic battery between two carbon points, diamonds swell up, become opaque, and are transformed into a material nearly resembling

plumbago. The inverse transformation has not yet been effected.

Plumbago, or black-lead, as it is commonly but very improperly called, is obtained from mines in Cumberland, Ceylon, and some other districts. A very similar substance is formed by the gradual cooling of large masses of cast-iron. The molten mass contains carbon in solution, and a part of this carbon crystallizes out on the surface of the iron while it is cooling. A very pure and dense variety of carbon is found in the roof of old gas-retorts, where it had been gradually deposited, by the action of the high temperature upon the coal-gas which was passing out.

55. Coke is a dense variety of carbon, prepared by heating coals to a bright red heat, and thereby expelling, as gas, oils, &c., all the hydrogen and oxygen of the native coal, with some of its carbon. Coals which are rich in compounds of hydrogen become semi-fluid before decomposition, and the coke which is left from them is in large coherent masses. Such coals are called caking coals. Welsh coal and anthracite contain little hydrogen, and burn with very little flame or smoke. They approach more nearly to the composition of coke than the bituminous coals. Coke generally contains earthy matter, which remains as an ash when the carbon is burnt away, and sometimes a good deal of sulphur in the form of ferric sulphide or pyrites, which diminishes its value considerably for foundry use.

Charcoal is the name given to the carbon obtained by expelling nearly all the hydrogen and oxygen from wood by heat, the necessary heat being usually obtained by burning some of the wood. The ashes of charcoal contain potassic carbonate. Few persons can have used successively coke and charcoal for fuel without noticing the comparative difficulty of lighting coke; inasmuch as those parts of it to which heat is applied allow the heat to escape from them into

the rest of the heap, far more rapidly than is the case with charcoal. This superior conducting power for heat which belongs to coke, is mainly owing to the comparatively dense state of aggregation of its particles, acquired by the high temperature to which they have been exposed; for if a piece of soft porous charcoal be heated to a good white heat in a closed vessel, it is found to become harder and more difficult of ignition than before, in fact very much like coke itself. At no temperature to which it has been exposed does carbon evaporate, or even shew signs of fusion.

56. When prepared at a comparatively low temperature charcoal possesses the power of condensing large quantities of gas on its surface, and the gas so condensed is capable of producing effects which it cannot produce under similar circumstances when uncondensed. Thus, the oxygen of atmospheric air when condensed by charcoal combines rapidly with all volatile combustible bodies which come in contact with it. Many of the most dangerous impurities in atmospheric air, such as the fetid products given off by putrefying animal or vegetable matter, can be removed from it completely by a process of total oxidation, by passing the impure air through a sufficient thickness of powdered charcoal. The air is thus rendered inodorous and harmless. **Respirators** have been constructed by Dr. Stenhouse, for purifying in this manner the air which passes into the lungs, and their efficacy is increased by a small quantity of finely-divided platinum spread over the charcoal. It is much to be regretted that this most valuable safeguard to health is not more generally known and adopted.

Animal charcoal, bone black, ivory black, &c., are names given to mixtures of carbon with calcic phosphate, obtained by heating bones in a closed vessel until the organic matter contained in them is completely decomposed, leaving charcoal intimately mixed with the incombustible materials of the

bones. The presence of the phosphate in this animal charcoal enables the carbon to remove various colouring matters from liquids, and the substance is accordingly much used by sugar-refiners and others for the purpose of decolorizing solutions. An exceedingly striking illustration of the action of animal charcoal is obtained by putting some of it, in the form of a fine powder, into water coloured deep blue by sulphindigotic acid. The colouring matter is speedily absorbed by the animal charcoal, and a colourless liquid is obtained by filtration. The charcoal obtained by calcining blood with potassic carbonate is found very efficacious for some purposes of decolorization.

Lamp-black is a fine powder of charcoal, usually contaminated by oily matter. It is made by burning hydrocarbons, such as turpentine, with a supply of air insufficient for their complete combustion. The smoke from these flames, or better still, from very bituminous coal, is made to pass through long horizontal flues, where the lamp-black gradually collects. Lamp-black, when mixed with linseed-oil and soap, forms printing-ink.

57. When heated to redness in contact with free oxygen carbon burns, forming carbonic acid. Dumas found that by burning diamonds in oxygen gas, 44 parts by weight of carbonic acid are formed from every 12 parts by weight of carbon. The compound is therefore represented by the formula CO_2.

When heated in carbonic acid, carbon also burns at the expense of the oxygen of that compound, $C + CO_2 = 2(CO)$; and when air passes up through a thick layer of red-hot charcoal or coal, there is a formation of carbonic acid at the bottom, but this carbonic acid in passing over the red-hot charcoal takes up carbon, and becomes reduced to carbonic oxide.

At very high temperatures carbon combines also with

hydrogen, forming the gaseous compound C^2H_2, called **acetylene**. This is obtained by discharging a powerful galvanic battery by carbon points, separated from one another by an atmosphere of hydrogen. With nitrogen, carbon does not combine without the intervention of other substances.

Steam at very high temperatures is reduced by charcoal, according to the equation—

$$C + H_2O = CO + H^2.$$

At a red heat carbonic acid is formed, as well as carbonic oxide.

Ammonia is also decomposed by charcoal at a red heat. The products of the action are free nitrogen, hydrogen, and ammonic cyanide (CN_2H_4).

Charcoal evolves 8,080 degrees of heat on burning to form carbonic acid. Only two compounds of carbon and oxygen are known, viz. carbonic acid and carbonic oxide.

58. Carbonic Acid gas (CO_2=2 vols.) is prepared by dissolving chalk or white marble in hydric chloride—

$$CaCO_3 + 2(HCl) = CaCl_2 + H_2O + CO_2.$$

Hydric sulphate is used instead of common hydric chloride, if carbonic acid be required for purposes in which the presence of a little arsenic would be injurious.

The gas is about half as heavy again as atmospheric air; its density being like that of nitrous oxide, 22, CO_2=2 vols.

$$C + \boxed{O=16} \quad \boxed{O=16} = \boxed{\frac{CO_2}{2}=22} \quad \boxed{\frac{CO_2}{2}=22}$$

It neither burns nor supports combustion, so that a lighted taper is extinguished when lowered into carbonic acid gas. It can be poured from one vessel to another by displacement of air, but should not be left long in an open vessel, as it gradually escapes by diffusion. Clear lime-water is

precipitated by carbonic acid, the precipitate being calcic carbonate.

When subjected to a pressure of 35.4 atmospheres, at the temperature of 0°C, carbonic acid is condensed into a liquid. At −25°C it only requires 17.2 atmospheres pressure for its condensation. The **liquid carbonic acid** is frequently prepared by putting hydro-sodic carbonate (often called bicarbonate of soda) and water into a strong wrought-iron bottle, together with a narrow pot nearly full of oil of vitriol. The bottle is closed by a screw-plug, and then agitated so as to shake the acid out of its pot, and bring it in contact with the carbonate.

Liquid Carbonic Acid is said to have a density of 0.9 at −20°C, and a density of 0.6 at 30°; so that a rise of temperature of 50° increases its volume about 50 per cent., or about three times as much as if it were a gas. The liquid acid is usually distilled out into another vessel before use. When brought out to the open air a portion of the carbonic acid boils so rapidly as to freeze the remainder into a white solid, looking very much like snow. An alcohol thermometer immersed in this solid carbonic acid falls to −78°C. The solid dissolves readily in ether, and can be most conveniently used in that form for freezing purposes. Metallic mercury is instantly frozen into a solid mass like lead by contact with the solution; and if it comes in contact with the skin, a blister is said to be produced very similar to that produced by a burn. The solid acid can, however, be taken up by the hand without producing any painful sensation, as it does not come in contact with the surface of the hand sufficiently to absorb much heat from it.

The specific heat of gaseous carbonic acid, between 10° and 200°C, is .2169. At the ordinary atmospheric temperature of 15°C water dissolves about its own volume of carbonic acid, and the solution has a slightly acid reaction

to litmus-paper. At 0°C the exact volume of carbonic acid absorbed by water is 1.7967; at 10°C it is 1.1847; at 20°C it is 0.9014. A piece of litmus-paper, reddened by the solution of carbonic acid, resumes its blue colour on exposure to the air for a few minutes, by evaporation of the acid. The aqueous solution no doubt contains **hydric carbonate** (CO_3H_2), although that compound has never been separated from the water.

59. Carbonic acid reacts in two distinct proportions upon potash, forming a normal carbonate called potassic carbonate (CO_3K_2), and a double salt hydro-potassic carbonate, often called bicarbonate of potash (CO_3HK). The former salt is decidedly alkaline in its reaction and properties, proving that carbonic acid is by no means capable of neutralizing two atoms of potassium. Even the second salt is slightly alkaline. Ammonia combines with carbonic acid, forming a solid and very volatile compound, well known by the name of volatile salt of hartshorn.

In the pure state the commercial salt has the composition $2(NH_4)_2O, 3CO_2$, and is called ammonic sesqui-carbonate[i].

[i] Among the oxides enumerated in § 18, all which are strong bases can be obtained in combination with carbonic acid. Thus, there are the following carbonates corresponding to the first class of oxides, viz.

Silver carbonate, Ag_2CO_3.	Sodio-potassic carbonate, $NaKCO_3$.
Potassic carbonate, K_2CO_3.	Sodic carbonate, Na_2CO_3.
Hydro-potassic carbonate, $HKCO_3$.	

The peroxides (2nd and 4th classes) do not possess basic properties, and they form no compounds with carbonic acid.

Many oxides of the third class form carbonates, such as—

Baric carbonate, $BaCO_3$.	Calcic carbonate, $CaCO_3$.
Strontic carbonate, $SrCO_3$.	Magnesic carbonate, $MgCO_3$.

Others, such as cupric oxide, cannot form regular or so-called normal carbonates, but when supplied with it in due proportion allow some of the acid to escape and form a compound of oxide and carbonate. Others, again, such as mercuric oxide, are unable to hold carbonic acid in combination.

Appendix to Chapter IX.

PROBLEMS.

55. What weight of air is needed for the complete combustion of 1 kilogramme of carbon?

56. A chamber contains 60 cubic metres of air at 14°C and 760 mm. pressure. 500 grammes of carbon are completely burnt in the room and nothing allowed to escape. What is the percentage composition of the residual mixture, assuming the original air to have consisted of 21 per cent. oxygen and 79 per cent. nitrogen by volume?

57. What weight of hydro-sodic carbonate, and what weight of hydric sulphate, must be used in order to evolve 1 kilogramme of carbonic acid according to the equation—

$$H\,Na\,C\,O_3 + H_2\,S\,O_4 = H\,Na\,S\,O_4 + H_2\,O + C\,O_2\,?$$

58. What volume of carbonic acid would be obtained by combining 100 grammes of oxygen in the proper proportion with carbon?

59. What weight of carbon is contained in a litre of carbonic acid?

60. What weight of calcic carbonate must be dissolved for the evolution of 20 litres of carbonic acid at 15°C and 760 mm. pressure?

CHAPTER X.

60. Carbonic Oxide (C O = 2 vols.) is most conveniently prepared in large quantities by passing dry carbonic acid through a red-hot tube containing charcoal, and then through a bottle containing pieces of coke soaked in potash. In most cases it is best made by mixing potassic formiate with oil of vitriol, in sufficient quantity to form a thin mud, and heating the mixture. The reaction which ensues is this—

$$C H K O_2 + S O_4 H_2 = C O + S O_4 H K + H_2 O.$$

Carbonic oxide is a little lighter than atmospheric air; its density being 14, the same as that of nitrogen. It burns in

$$C + \boxed{O = 16} = \boxed{\frac{CO}{2} = 14} \quad \boxed{\frac{CO}{2} = 14}$$

air with a pale blue flame, forming carbonic acid, and every two volumes of carbonic oxide combine with one volume of oxygen to form two volumes of carbonic acid. When the

$$\boxed{\frac{CO}{2} = 14} \quad \boxed{\frac{CO}{2} = 14} + \boxed{O = 16} = \boxed{\frac{CO_2}{2} = 22} \quad \boxed{\frac{CO_2}{2} = 22}$$

mixture in these proportions is fired by the electric spark it explodes with force about equal to that of the explosion of oxy-hydrogen gas. The **heat of combustion of carbonic**

oxide is 2,403 degrees, that is, 1 gramme of carbonic oxide evolves 2,403 degrees of heat, therefore the weight of carbonic oxide which contains 1 gramme of carbon evolves 5,607 degrees of heat on taking up the additional oxygen to form carbonic acid. If this quantity of heat be deducted from 8,080 degrees, which charcoal gives off when it burns to carbonic acid, the difference, namely $8080 - 5607 = 2473$, shews how much heat is evolved by one part by weight of carbon burning to form carbonic oxide.

61. Some **furnaces** are occasionally to be seen at work under such conditions that the air, after forming carbonic acid with the fuel with which it first comes in contact, is then forced over red-hot coals, so as to reduce this carbonic acid to carbonic oxide, which escapes unburnt or burns outside the furnace: and the above calculation shews that in such cases there is less than one-third the total quantity of heat of combustion of the fuel given off in the furnace. To rectify the working of such a furnace the mixture of nitrogen and carbonic oxide which passes out from the coals should be intimately mixed, while still hot, with as great a volume of air as that which passed through the coals.

The weight of air needed for burning completely 1 kilo. of coal is nearly 12 kilos., and these occupy at the common temperature about $9\frac{3}{4}$ cubic metres. To verify these numbers we should first calculate the weight of oxygen needed to burn a kilo. of coal, and then how much air must be taken in order to supply the needful quantity of oxygen. The formula CO_2 shews that for every 12 parts by weight of carbon 33 parts by weight of oxygen are needed, or for one of carbon $2\frac{2}{3}$ of oxygen. As air contains 23 per cent. of oxygen by weight, we have the proportion $23 : 100 = 2\frac{2}{3} : x$, whence 11.56 kilos. is the weight of air needed to burn 1 kilo. of carbon. Coals, however, usually contain some unburnt hydrogen, and this renders a greater proportion of oxygen necessary; so that

12 kilos. of air is by no means too much to allow. Allowing 1.293 kilo. as the weight of a cubic metre of air at 0°, or 1.2256 at 15°C, the proportion $1.2256 : 1 = 12 : x$ gives us 9.7584, or in round numbers $9\frac{3}{4}$, as the number of cubic metres of air at 15° weighing 12 kilos., needed for the combustion of 1 kilo. of coal.

62. The **specific heat of carbonic oxide** is .2450. When it combines with oxygen the carbonic acid formed would have a specific heat equal to .235 if it retained that of the oxygen and of the carbonic oxide without loss, whereas the specific heat of carbonic acid is only .2103. Carbonic oxide has never been condensed by cold or pressure into a liquid. Carbonic oxide is stated to be poisonous when taken into the lungs for some time, and the deadly effects produced by a charcoal fire in an unventilated room are attributed to its action. It is rather less soluble than oxygen in water. A solution of potash does not absorb it in the cold, but carbonic oxide is slowly absorbed by semi-fluid potash at 100°C, producing potassic formiate—

$$C O + H K O = K C H O_2.$$

Carbonic oxide is absorbed by a solution of cuprous chloride ($Cu^2 Cl_2$) in aqueous hydric chloride. Melted potassium also absorbs carbonic oxide.

63. Oxalic Acid ($C^2 O_3$) is not known in the free state. Its salts are contained in the juice of many plants, such as sorrel, lichens, &c. Its compound with water (hydric oxalate, $H_2 C^2 O_4$), generally called oxalic acid, is now prepared on a large scale by heating sawdust with a mixture of potassic and sodic hydrate. The alkaline oxalates thus obtained are dissolved in water and boiled with milk of lime. The lime carries down the acid as insoluble salt, and the alkaline hydrates are left in solution ready for using with some fresh sawdust as soon as they have been boiled down—

$$Na_2 C^2 O_4 + Ca O_2 H_2 = 2 (Na O H) + Ca C^2 O_4.$$

The calcic oxalate is decomposed by dilute hydric sulphate—

$$Ca\,C^2\,O_4 + H_2\,S\,O_4 = H_2\,C^2\,O_4 + Ca\,S\,O_4.$$

Hydric oxalate may easily be made on a small scale by the action of nitric acid on sugar or starch. Eight parts of nitric acid of 1.37 density are heated with one part of sugar, and the mixture evaporated to about $\frac{1}{6}$ of its original volume, when crystals of the hydrogen salt are deposited on cooling.

The crystals contain two molecules of water—

$$C^2\,H_2\,O_4\,(H_2\,O)_2,$$

which can be expelled by gentle heat, and a white powder is then left consisting of the hydrogen salt $H_2\,C^2\,O_4$.

When heated more strongly the salt decomposes chiefly into carbonic acid and carbonic oxide, whilst water is liberated,

$$C^2\,H_2\,O_4 = C\,O_2 + C\,O + H_2\,O;$$

but a small quantity of the compound is carried up by the escaping gases, and condenses on any cold surface over which it is led, whilst a little formiate is formed at the same time.

When an oxalate is heated with strong hydric sulphate it breaks up entirely into carbonic acid and carbonic oxide, whilst water is liberated—

$$C^2\,H_2\,O_4 = C\,O_2 + C\,O + H_2\,O.$$

When hydric oxalate is heated to a temperature of 100° with glycerine, it breaks up entirely into hydric formiate and carbonic acid—

$$C^2\,H_2\,O_4 = C\,O_2 + C\,H_2\,O_2.$$

64. Hydric oxalate dissolves readily in water, and has an intensely acid taste, and acid reaction to litmus-paper. Its solution expels carbonic acid from its salts, whilst water is formed at the same time, and it destroys the alkaline reaction of potash and soda. With either of these bases it reacts in two distinct proportions, forming first a double salt of hydrogen and potassium—

$$H_2\,C^2\,O_4 + K\,O\,H = H\,K\,C^2\,O_4 + H_2O;$$

or, with twice as much base, it forms the normal potassic oxalate—

$$H_2C^2O_4 + 2(KOH) = K_2C^2O_4 + 2(H_2O).$$

There is also another double salt containing hydrogen and potassium, tri-hydro-potassic binoxalate, $H_3KC^4O_8$.

Ammonia combines with hydric oxalate to form either a neutral ammonic oxalate, $(NH_4)_2C^2O_4(H_2O)$, or hydr-ammonic oxalate, $H(NH_4)C^2O_4(H_2O)$.

The **salts of oxalic acid**, containing calcium, barium, or the heavy metals, such as zinc, iron, lead, &c., are insoluble in water, but soluble in acids. One of the most important of its salts is the **calcic oxalate** (CaC^2O_4), which is insoluble in water and in hydric acetate, though soluble in hydric chloride or nitrate. When the salt is cautiously heated it decomposes, leaving a colourless residue of calcic carbonate, whilst carbonic oxide escapes. The residue dissolves with effervescence in hydric acetate. When mixed with manganic peroxide, in presence of hydric chloride, the oxalic acid in oxalates is completely oxidized to carbonic acid.

Commercial oxalic acid generally contains some mineral impurities, which are left as an ash when the acid is burnt. If it be required in a state of purity it should be made from distilled vinic oxalate, which is easily decomposed by water.

65. Formic Acid ($C^2H_2O_3$) is not known in the free state. Its hydrogen salt, CHO_2, was originally extracted from red ants, and was named from that source. It is formed by the partial oxidation of a great variety of organic bodies, such as sugar, gum, tartaric acid, alcohol, &c.; but by far the best way of making it is by the action of glycerine on dried oxalic acid. A tubulated retort is about one-quarter filled with concentrated glycerine, and as much dry oxalate thrown in as the glycerine can cover. The mouth of the retort is inserted into a flask receiver, and its body is surrounded by boiling water. The formiate distils over into the

receiver, whilst carbonic acid escapes; and when it ceases to come over some fresh oxalate is put into the retort, and the process is thus repeated with the same portion of glycerine until enough acid has been collected. If the compound be required free from uncombined water, it should be made by the action of sulphuretted hydrogen on dry plumbic formiate—

$$Pb(CHO_2)_2 + H_2S = PbS + 2(CH_2O_2).$$

It is then obtained as a liquid of 1.235 density, and boiling at 100°.

Compounds of formic acid greatly resemble those of acetic acid (or vinegar) in their properties. One of the least soluble of the formiates is the plumbic salt. With calcium it forms an exceedingly soluble salt, obtained by dissolving lime in hydric formiate—

$$CaO + 2(HCHO_2) = H_2O + Ca(CHO_2)_2.$$

Mercuric and argentic formiates are completely decomposed by heat in presence of water, the metal being reduced and carbonic acid making its escape with effervescence. Formic acid resembles nitric acid in reacting on potash in one proportion only, forming the salt $KCHO_2$, containing one atom of potassium in the place of one atom of hydrogen in the hydrogen salt. This neutral salt forms an unstable compound with the acid hydrogen salt, having the composition $(KCHO_2)(HCHO_2)$; but this substance is a very unstable chemical compound, for the hydric formiate contained in it is driven off at 100°, just like free hydric formiate.

There are many compounds of carbon and hydrogen, but only one of them (acetylene) has been made by the direct combination of the elements. Several hydrocarbons are gaseous, many are liquid, and some, as paraffine, are solids. The three simplest hydrocarbons will alone be described at present; and first of these marsh gas.

Appendix to Chapter X.

PROBLEMS.

61. What volume of carbonic acid must be passed over white-hot charcoal for the preparation of 10 litres of carbonic oxide?

62. What volume of carbonic oxide will be obtained by passing a litre of oxygen over an excess of white-hot charcoal?

63. 10 litres of a mixture of carbonic oxide and oxygen, in the combining proportions, are fired by the electric spark. What volume of carbonic acid is formed?

64. A ton of carbon has to be burnt to carbonic oxide by means of air. What volume of air is needed for the purpose? What will be the volume of the mixture formed? How much heat will be evolved in the process? How much heat will be obtained by burning the carbonic oxide?

65. What weight of water, supplied at 0°C, would be evaporated at atmospheric pressure by the total heat of combustion of 1 kilogramme of carbon?

66. How much heat is evolved by the combustion of a litre of carbonic oxide, measured at 0°C and 760 mm.?

67. 50 grammes of crystallized 'oxalic acid' are decomposed by sulphuric acid. What volume of carbonic oxide is evolved?

68. What weight of ammonia would be neutralized by a kilogramme of hydric oxalate ($H_2C^2O_4$)?

69. What weight of pure hydric formiate would be formed from a kilogramme of hydric oxalate by the action of glycerine? and what weight of ammonia would this formiate neutralize?

CHAPTER XI.

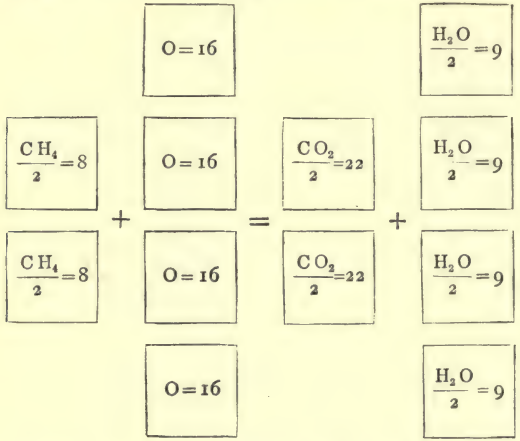
66. Marsh Gas (CH_4=2 vols.). It is formed by the putrefaction of vegetable matter under water, and has thence obtained its name. It is also given off in coal mines, and by mixing with air in the shafts and galleries gives rise to an explosive mixture, which it is the duty of the superintendent to remove by thorough ventilation, before it accumulates in sufficient quantity to do harm.

Marsh gas is formed by the action of a high temperature on many volatile and fixed organic bodies, and is a chief constituent of coal gas; but the most convenient way to prepare it for use is, to mix potassic acetate with two or three times its weight of slaked lime, and to heat the mixture in a flask coated with Stourbridge clay. Marsh gas is given off below a red heat, and carbonic acid remains in combination with the bases, partly potash, partly lime. The product requires purification by oil of vitriol. The equation

$$C^2H_3KO_2 + HKO = CH_4 + CO_3K_2$$

represents the process, assuming potassic hydrate to react on the acetate. Marsh gas burns with a yellowish blue flame, but if previously heated by passing through a red-hot tube it is said to yield a far more luminous flame. One molecule of the gas, occupying two volumes, requires four atoms of oxygen, occupying four volumes, for its complete combustion, and the mixture explodes even more strongly than oxy-hydrogen gas. The products are two volumes of carbonic acid, four volumes of steam, of which latter the

greater part condenses at the ordinary temperature and pressure. Marsh gas is the lightest known substance, next to hydrogen—its density being only 8. All attempts to con-



dense marsh gas, by combined cold and pressure, have failed. Marsh gas is rather more soluble than oxygen in water, for at 0°C one volume of water dissolves 0.054; at 10°C 0.044; and at 20°C 0.035.

A succession of electric sparks decomposes marsh gas, carbon being deposited, and hydrogen being left, of volume double the marsh gas employed.

67. Ethylene or **Olefiant Gas** ($C^2H_4 = 2$ vols.) is one of the minor constituents of coal-gas. It is best made by heating spirits of wine with about double its bulk of strong hydric sulphate. Some dry sand should be added, in sufficient quantity to form a thick mud with the mixture, as it is otherwise liable to froth very much. The gas comes over with water, which is formed at the same time, by decomposition of the alcohol—

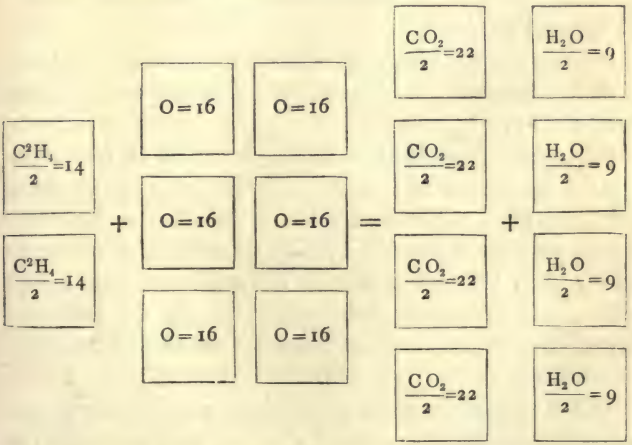
Alcohol, $C^2H_6O = C^2H_4 + H_2O$.

Some alcohol vapour is also carried over, as well as ether, and these impurities are best removed by passing the gas through oil of vitriol spread over pumice-stone. There is also sulphurous acid and carbonic acid formed, by the combustion of some of the alcohol at the expense of the sulphate, and to remove these impurities the gas should be passed through caustic potash. It is then obtained as a colourless and nearly inodorous gas, of the same density as nitrogen and carbonic oxide, viz. 14.

Olefiant gas dissolves considerably in water. One volume at 0°C dissolves 0.256 of the gas, at 10°C 0.184, and at 20°C 0.149.

Faraday compressed olefiant gas to a liquid, by using a very great cold, together with pressure. At −76°C the liquid was found to exert a pressure of 4.6 atmospheres, and at −17.8°C as much as 26.9 atmospheres.

Olefiant gas burns with a bright luminous flame, consuming



in the process three times its own volume of oxygen, and forming twice its own volume of carbonic acid. It is easily

decomposed by heat, and if passed through a red-hot tube, it deposits carbon and forms marsh gas, together with other compounds; but at very high temperatures the marsh gas is in its turn decomposed, liberating hydrogen.

Olefiant gas is rapidly absorbed by sulphuric acid ($S O_3$), or by the fuming sulphuric acid (hydric disulphate), which is a compound of the acid with the hydric sulphate, and this re-agent is usually employed for absorbing olefiant gas in any mixture, such as coal gas, in which its quantity has to be determined. It is also absorbed, though very slowly, by common oil of vitriol (hydric sulphate), and the compound thus formed is a double salt of ethyle ($C^2 H_5$) and hydrogen. By mixing this double salt with water, and boiling the mixture, alcohol is distilled over, thus—

$$(C^2 H_5) H S O_4 + H_2 O = S O_4 H_2 + C^2 H_6 O.$$

Through the agency of sulphuric acid, alcohol can therefore be built up again from olefiant gas and water, the very products into which it is decomposed, at a high temperature, by the acid itself.

Olefiant gas has obtained its name from the circumstance of its forming with chlorine an oily compound called **Dutch liquid** ($C^2 H_4 Cl_2$).

68. Acetylene ($C^2 H_2 = 2$ vols.) is said to be formed by passing the vapour of Dutch liquid through a red-hot tube. It burns with a rather smoky flame. Its most characteristic property is that of forming a solid compound of a red-brown colour when led into a solution of cuprous chloride in ammonia. This compound is explosive. By the action of hydric chloride the compound is decomposed with liberation of acetylene.

When warmed in contact with zinc, in a solution of ammonia, it gradually combines with the hydrogen which is being given off, and forms olefiant gas.

69. Coal-Gas is a mixture of gaseous compounds given

off by coals, when rapidly heated to redness in an iron or earthenware retort. The quality of coal used for preparing gas is by no means a matter of indifference. The resinous coals yield far more gas than those harder varieties which do not cake on heating. **Anthracite** is of all kinds the most useless for gas making, as it approaches most nearly to coke in its composition. Cannel coal, and especially a substance known by the name of Boghead Cannel, are the best gas coals, a ton of these yielding as much as 15,000 cubic feet of gas. Ordinary varieties of blazing coal yield from 8,000 to 11,000 cubic feet per ton.

70. The gas deposits a good deal of semi-fluid matter known by the name of tar, together with water containing ammoniacal compounds. **Coal-tar** is alkaline to test-paper, and hydric chloride dissolves out from it a mixture of basic compounds, containing carbon, hydrogen, and nitrogen, bases which can be precipitated from their solution in hydric chloride by potash, in the form of heavy oils.

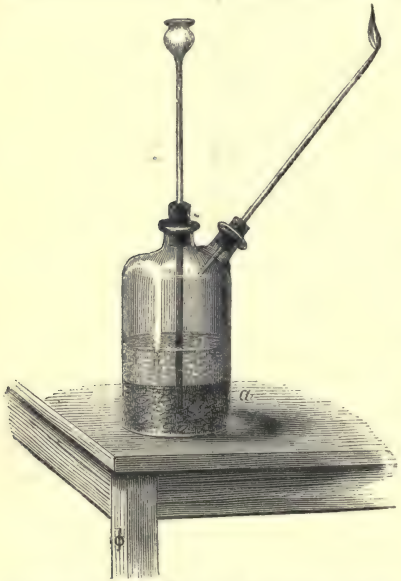
The difference between coal-tar and wood-tar is worthy of note, for whereas the former is alkaline, the latter is strongly acid. This is explained by the fact that wood contains a large proportion of oxygen, which during the formation of coal has been given out in combination with carbon, as carbonic acid.

Coal-tar also contains oily acids, which can be dissolved out from it by lime, and which are precipitated by hydric chloride. These are used for preserving meat and timber and other organic bodies from putrefaction and decay, and are generally called coal-tar **creosote.** One chief antiseptic constituent of creosote is a crystalline body of the composition $C^6 H_6 O$, a kind of alcohol called **phenylic hydrate** or phenol.

Besides these basic and acid oils, coal-tar contains several neutral oils and crystalline compounds. Among these

benzole (C^6H_6) and **naphthaline** ($C^{10}H_8$) deserve special mention. The former is the material from which aniline is artificially prepared for the manufacture of dyes, and the latter is a volatile solid which contributes materially to the peculiar smell of coal-gas.

71. After it has deposited the tar, coal-gas has to be purified before use. The worst impurity which it contains is sulphur, and this element is present partly in the form of sulphuretted hydrogen (SH_2), partly in the form of carbonic sulphide (CS_2). The former is removed by passing the gas over ferric hydrate, iron combining with the sulphur and water being formed. The carbonic sulphide is left in the gas for want of a convenient method of removing it.



Apparatus to shew flame of Hydrogen charged with Benzole.—*a* Bottle containing zinc and dilute acid.

Ammonia should also be removed as completely as possible from the gas, not only for the sake of its commercial value for agricultural and other purposes, but also because it corrodes the brass tubes through which gas is passed. Trays filled with sawdust soaked with dilute hydric sulphate are used for this purpose.

72. The greater portion of the volume of coal-gas consists

of hydrogen and marsh gas, the former of which evolves heat and scarcely any light on combustion, while the latter is of very small illuminating value. In spite of this, hydrogen itself contributes to the illuminating value of coal-gas, by keeping in it the vapour of benzole and of other highly illuminating liquids. A very simple experiment may prove this, for if a jet of hydrogen, which is burning at a fine point, be supplied with benzole, by pouring a few drops of the oil into the bottle in which the gas is being evolved, the flame immediately becomes white, or sometimes even smoky. Hydrogen and marsh gas are therefore of value by serving to carry the vapour of benzole, or when present in the gas from Boghead Cannel they aid the evaporation of hydrocarbons, such as amylic hydride, C^5H_{12}. Carbonic oxide is a minor constituent of coal-gas, which has a similar value. The actual illuminating body contained in coal-gas is olefiant gas, of which there is generally three to four per cent. of the volume of the mixture. In some varieties of gas there is besides olefiant gas a more easily condensible hydrocarbon, containing carbon and hydrogen in the same proportion as olefiant gas, but differing from that body by its density, which is twice as great—viz. 28. This can be seen from its formula—$C^4H_8 = 2$ vols. This gas is often named after its illustrious discoverer, Faraday's gas. It is also called **butylene**.

Carbonic acid and nitrogen are generally present in gas, in very small quantities. As an example of a coal-gas, the following result of an analysis of a Manchester gas by Bunsen may be quoted. The numbers represent volumes of each constituent in 100 volumes of the gas.

Hydrogen	45.58	Butylene	2.38
Marsh gas	34.90	Sulphuretted hydrogen	0.29
Carbonic oxide	6.64	Nitrogen	2.46
Olefiant gas	4.08	Carbonic acid	3.67

Acetylene is also frequently contained in coal-gas.

73. Structure of flame. A burning candle or oil lamp differs from a flame of gas mainly in one respect; namely, that it is a gas manufactory as well as a gas burner. For the liquid fat or oil is drawn up by the wick, in the midst of the flame, where it is made into gas by the action of heat, and the gas burns all round the wick as fast as it is formed, evolving (by its combustion) heat, which keeps up the supply of gas. Immediately round the wick of a candle the flame does not give light. This dark zone extends usually to some height above the wick. It consists of combustible gases, on their way from the wick to the outer part of the flame, where they get burnt.

Immediately round this inner and non-luminous zone is the brighter part of every flame. It consists mainly of steam, formed by the combustion of hydrogen, and solid particles of carbon, heated to a bright white heat. Of course nitrogen penetrates into it, with the oxygen which goes to form steam. A clear bead of glass held in this part of the flame by a platinum wire or forceps gets blackened by collecting soot, and metallic oxides—such as plumbic oxide—which part with their oxygen easily are reduced to the metallic state. This flame, containing free carbon, is therefore called the **reducing flame**.

The outer surface and the top of the flame is usually of a pale blue or violet colour, and consists of carbonic acid and steam, mixed with nitrogen and heated to a high temperature by the complete combustion of the gas. This outer flame is called the **oxidizing flame**, as it produces powerful effects of oxidation, owing to the presence in it of atmospheric air, at a high temperature.

Whenever hydrocarbons are imperfectly burnt, there is a deposition of carbon, as the more active hydrogen gets oxidized first; and this temporary deposition of carbon is an essential condition for the production of the white light required in an ordinary flame.

When coal gas is wanted for heating purposes it can be burnt in **Bunsen burners**, which are so constructed that the coal-gas mixes in a tube with a certain limited quantity of air, and the mixture burns in the open air on coming out of this tube. Under these circumstances a pale violet colour is alone visible in the flame, and it is scarcely more luminous than a similar flame of hydrogen. When a more intense heat is needed, the flame is supplied by a jet of air from the nozzle of a mouth **blow-pipe**, or, better still, a blow-pipe worked by bellows; and in this manner glass tubes or rods can be readily heated so as to bend to any required angle, or so as to be drawn out to a fine point.

Appendix to Chapter XI.

PROBLEMS.

70. What is the weight of 10 litres of marsh gas at 0°C and 760 mm.?

71. What volume of air is needed for the complete combustion of a litre of marsh gas? What will be the volume (calculated at 0°C and 760 mm.) of the steam formed by its combustion?

72. What weight of marsh gas would be obtained from a kilogramme of potassic acetate, according to the equation

$$K C^2 H_3 O_2 + K H O = C H_4 + K_2 C O_3 ?$$

73. What is the volume of a kilogramme of ethylene?

74. What volume of oxygen is needed for the complete combustion of a litre of ethylene? What volume of carbonic acid, and what volume of steam, are formed?

75. What volume of hydrogen would be obtained from a litre of ethylene if the carbon were entirely removed?

76. What volume of acetylene could be burned by a litre of oxygen? What would be the volumes of the products?

77. What is the weight of a litre of acetylene?

78. A thousand litres of ethylene are burned in a chamber containing 100 cubic metres of dry and pure air, both at 0°C and 760 mm. What is the percentage composition of the air at the end of the process, supposing nothing to escape or enter?

CHAPTER XII.

74. Cyanogen[k] ($C^2N_2 = 2$ vols.) is best prepared by heating mercuric cyanide in a glass tube. It should be collected over mercury, or by displacement of air, as water dissolves it to a considerable extent. Metallic mercury is set free, together with cyanogen gas; at the same time a dark brown mass containing carbon and nitrogen is formed.

Cyanogen is a heavy gas of pungent odour. Its density is 26. It burns with a purple flame, combining with twice its bulk of oxygen. When passed through a tube cooled to a temperature of $-25°C$ to $-30°C$ it condenses to a liquid, and at $0°C$ the liquid was found by Bunsen to exert a pressure of 2.7 atmospheres; at $20°C$ of 5 atmospheres. The liquid freezes at $-34.4°C$. When dissolved in water cyanogen speedily decomposes, forming a variety of products; amongst which is ammonic oxalate, formed by the following reaction,

$$C^2N_2 + 4(H_2O) = C^2(NH_4)_2O_4.$$

Cyanogen combines with potassium, but the compound (KCN) is easily decomposed by acid compounds in presence of water. Cyanogen is remarkable for the stability of the double salt, which it forms with iron and potassium, and for the instability of its compounds with the alkali metals. With iron it forms the valuable blue colours known by the name of Prussian blue.

75. Cyanides (HCN = 2 vols.). The symbol Cy is

[k] $Hg(CN)_2 = Hg + C^2N_2$.

sometimes used for an atom of cyanogen, Cy=C N. H Cy is then the formula for the cyanide. Hydric cyanide, commonly called **prussic acid**, is most conveniently prepared by adding dry calcic chloride gradually to the aqueous solution of the acid, until considerably more is added than the liquid can dissolve, and then distilling the mixture at a very gentle heat, using as a condenser a vessel surrounded by a freezing mixture. In the dry state, as thus obtained, prussic acid is so exceedingly dangerous a substance, that it ought never to be made without a very good reason, and extreme care. It is a light mobile liquid, which boils at about 27°C, and evaporates in large quantities far below its boiling-point. A small quantity of the vapour is sufficient to produce instantaneous death. It burns easily in the air, combining with $1\frac{1}{4}$ times its volume of oxygen in the process.

It is dissolved by water in all proportions, but is held with very little force, so that even when diluted with much water the acid evaporates very easily.

To prepare a solution of **prussic acid** the usual plan is to decompose a solution of potassic ferro-cyanide by dilute hydric sulphate, and distil with a good condenser, and some cold water in the receiver. The best proportions are: 10 grammes of the crystallized ferro-cyanide dissolved in 50 grammes of water; 3.5 grammes of common oil of vitriol are then mixed with 25 grammes of water, and the mixture when cold is poured into the solution of the salt. On distilling this mixture a greenish white precipitate is formed, containing half the cyanogen of the salt employed, in combination with all the iron and one-quarter of the potassium.

The reaction is thus stated by equation—

$$2(Fe K_4(C N)_6) + 3(H_2 S O_4) + Aq = Fe_2 K_2(C N)_6 + \\ + 3(K_2 S O_4) + 6(H C N) + Aq.$$

The solution of prussic acid has a strong smell of the cyanide. It reddens litmus-paper very slightly indeed; has

so little tendency to take potassium in place of its hydrogen that it is not even able to decompose a solution of potassic carbonate. When mixed with a solution of potash, prussic acid is decomposed, forming potassic cyanide and water—

$$CNH + HKO = CNK + H_2O;$$

but the solution is as alkaline to test paper as caustic potash itself. It is decomposed by the carbonic acid contained in the air or breath: thus,

$$CNK + CO_3H_2 = CNH + CO_3HK;$$

hence the smell of prussic acid which it possesses[1].

A solution of prussic acid is liable to undergo decomposition, especially when exposed to the sunshine. A small quantity of hydric chloride impedes the decomposition, and is therefore usually added to prussic acid in order to preserve it; but concentrated hydric chloride decomposes the cyanide speedily, forming ammonic chloride and hydric formiate: thus,

$$CNH + 2(H_2O) + HCl = NH_3HCl + CH_2O_2.$$

When prussic acid is boiled with an excess of potash, ammonia is evolved, and potassic formiate remains in solution. Strong hydric sulphate not only acts like hydric chloride, in decomposing prussic acid, but when heated with the products causes a secondary decomposition of the formiate into carbonic oxide and water. The action of heat upon ammonic formiate gives rise to prussic acid and water,

$$(CNH_4HO_2 - 2(H_2O) = CNH).$$

[1] The following table shews the similarity of constitution between metallic cyanides and the corresponding chlorides—

Potassic cyanide, K C N.	Potassic chloride, K Cl.
Sodic cyanide, Na C N.	Sodic chloride, Na Cl.
Argentic cyanide, Ag C N.	Argentic chloride, Ag Cl.
Mercuric cyanide, $Hg(CN)_2$.	Mercuric chloride, $HgCl_2$.
Ferrous cyanide, $Fe(CN)_2$.	Ferrous chloride, $FeCl_2$.
Plumbic cyanide, $Pb(CN)_2$.	Plumbic chloride, $PbCl_2$.
Auric cyanide, $Au(CN)_3$.	Auric chloride, $AuCl_3$.
Platinic cyanide, $Pt(CN)_4$.	Platinic chloride, $PtCl_4$.

Prussic acid is recognized by a variety of tests, which are characteristic and delicate. When added to argentic nitrate it forms a precipitate consisting of argentic cyanide, and this precipitate dissolves in ammonia or in boiling nitrate, but not in cold dilute nitrate.

The best method of applying this test is to cover the glass vessel containing the very dilute solution of hydric cyanide with a glass plate, on the under side of which a drop of argentic nitrate has been placed. The cyanide evaporates and causes a cloudiness in the drop, owing to the formation of argentic cyanide.

With a solution of mercurous nitrate it forms a grey precipitate consisting of metallic mercury, whilst mercuric cyanide remains in the solution.

When neutralized by potash and heated with a solution of ferrous sulphate it forms potassic ferro-cyanide, which can be separated by filtration from ferric oxide and detected by acidulation with hydric chloride, and addition of ferric chloride, which precipitates Prussian blue.

By evaporation to dryness with yellow ammonic sulphide, prussic acid combines with sulphur and ammonia, and the residue, dissolved in water, gives a deep blood-red colour when mixed with ferric chloride—

$$6(NH_4CNS) + Fe^2Cl_6 = Fe^2(CNS)_6 + 6(NH_4Cl).$$

Ammonic sulphocyanate can also be obtained by the action of an excess of aqueous ammonia on carbonic sulphide—

$$CS_2 + 4(NH_3) = CNSNH_4 + S(NH_4)_2.$$

Potassic sulphocyanate (KCNS) is most easily obtained by fusing the cyanide with sulphur. It is remarkable for not decomposing in contact with water like potassic cyanate. It is used as a test for ferric salts.

76. Cyanic Acid is assumed to exist in the so-called cyanates, represented by hydric cyanate (HCNO). When

potassic cyanide is heated in contact with air, it combines with oxygen, forming potassic cyanate (K C N O), a salt of similar constitution to the sulphocyanate, but containing oxygen in place of sulphur. The hydric salt is prepared by distilling hydric cyanurate or cyamelide, and collecting the distillate in a well-cooled receiver. It is a very volatile liquid, of pungent odour and violent action on the skin. Even at the temperature of 0°C this compound speedily changes into a solid inert substance, called cyamelide; but at the ordinary atmospheric temperature the change is complete in five minutes. When dissolved in water, cyanic acid is recognized for a short time by its peculiar odour, but it soon combines with the elements of water, and becomes converted into hydr-ammonic carbonate—

$$C N O H + 2 (H_2O) = C O_3 H (N H_4).$$

77. Urea ($C O N_2 H_4$) is a weak basic compound contained in human urine, and constituting the chief nitrogenized excretion. It can be obtained by adding hydric nitrate to urine, previously evaporated to a small bulk. Impure crystals of urea nitrate are thus deposited, from which urea can be obtained by evaporating their solution in water to dryness with baric carbonate in slight excess, and dissolving out the urea by alcohol, which leaves baric nitrate undissolved.

Urea contains the elements of ammonic cyanate—

$$N H_4 (C N O);$$

and this suggested to Wöhler the possibility of making it artificially by combining ammonia and hydric cyanate. The usual plan is to mix a solution of potassic cyanate in water with ammonic sulphate, and to evaporate the mixture to dryness. The quantity of sulphate should be sufficient to supply fully as much sulphuric acid as the potassium in the cyanate requires. Alcohol is added to the dry mixture, and dissolves out urea from it, leaving potassic sulphate and the excess of

the ammonia salt. The process consists in an interchange of bases, between the potassic cyanate and ammonic sulphate, forming ammonic cyanate and potassic sulphate—

$$2(KCNO) + (NH_4)_2SO_4 = K_2SO_4 + 2(NH_4CNO);$$

part of the ammonia salt being changed into urea, while another part forms neutral ammonic carbonate by combining with water. By evaporation of its solution urea is obtained in the form of white needle-shaped crystals, which dissolve readily in water.

Urea nitrate is considerably less soluble in water than the base itself. Its composition is represented by the formula $(NO_3H)\,CN_2H_4O$. Nitrous acid immediately decomposes urea with effervescence; carbonic acid and nitrogen being given off whilst water is formed. When mercuric nitrate is added to a solution of urea, a white precipitate is formed, containing urea combined with mercuric oxide and a part of the nitric acid.

Urea oxalate is precipitated when a concentrated aqueous solution of urea is mixed with oxalic acid. Its formula is $(CN_2H_4O)_2H_2C^2O_4$. In contact with decomposing animal or vegetable matter urea combines with the elements of water, and is transformed into ammonic carbonate. Hence the presence of that salt in decomposed urine—

$$CON_2H_4 + 2(OH_2) = CO_3(NH_4)_2.$$

Urea is decomposed by heat. It first melts, and then gives off ammonia. When as much ammonia as possible has been expelled by heat, the residue possesses the composition of hydric cyanate or cyamelide, but different properties from either of these bodies. It is called 'cyanuric acid.'

Sulphur urea (CSN_2H_4) has lately been obtained by a process similar to that employed in obtaining ordinary urea by Wöhler's method, using ammonic sulphocyanate in place of the cyanate, but in consequence of the greater stability of

the former body, it has to be heated to a temperature above 180°C.

78. Cyanurates.—The hydrogen salt $H_3C_3N_3O_3$ is a solid crystallizable compound of great stability. It is purified by dissolving in oil of vitriol with the aid of heat, and adding hydric nitrate as long as there is any effervescence. Water then precipitates a snowy-white powder, which is pure cyanurate. A solution of cyanurate in water does not decompose like the corresponding solution of a cyanate.

The basic metal in cyanurates is replaceable in three proportions, forming double salts of the three following classes; viz. 1st, those in which one atom of hydrogen is replaced by the more basic metal, for instance, $KH_2C_3N_3O_3$; 2nd, salts which are formed by the substitution of metal for two atoms of hydrogen, such as $HAg_2C_3N_3O_3$; and, finally, salts in which all the three atoms of hydrogen are replaced by basic metal, such as $Ag_3C_3N_3O_3$. This shews that the molecule of the hydrogen salt contains three atoms of hydrogen.

Hydric cyanate has only one atom of hydrogen in each molecule, for we cannot remove a part of the hydrogen in one molecule without removing the whole.

Hydric cyanurate is converted into the cyanate by mere distillation, without taking up or losing anything; and cyamelide can be transformed in like manner into hydric cyanate without any change in the proportions of the elements contained in it.

79. The term '**isomerism**' is used to denote the existence of differences of physical or chemical properties among bodies of the same composition. When two compounds have the same percentage composition but different molecular weights they are frequently called '**polymeric**.' A fourth substance of considerable importance is isomeric with these three, viz. **hydric fulminate**. This body is only known in its salts,

the fulminates, of which the commonest is the mercury salt, a detonating compound used for charging percussion caps.

The salt is made by the action of nitrous acid on alcohol, in presence of a salt of mercury, and the violence with which it detonates when struck or heated finds no parallel in the case of any other of the isomeric bodies. Argentic fulminate is represented by the formula $Ag_2C_2N_2O_2$; and there is a double salt containing silver and potassium according to the proportions $AgKC_2N_2O_2$, which leads to the inference that the hydrogen salt itself, if prepared, would be found to possess the composition $H_2C_2N_2O_2$.

We have therefore the series of salts—

Cyanate	$HCNO$,
Fulminate	$H_2C_2N_2O_2$,
Cyanurate	$H_3C_3N_3O_3$.

80. Methylia (CNH_5). In the presence of spongy platinum prussic acid vapour combines with hydrogen, forming a compound wonderfully like ammonia in its properties, and called methylia. This remarkable base will be more fully described hereafter. Its vapour has the same power of saturating acid salts as an equal volume of ammonia, and CNH_5 may be considered equivalent to NH_3. Methylia can be condensed to a liquid at the atmospheric pressure, at a temperature but little below 0°C. Its vapour burns easily, forming carbonic acid and water, and liberating nitrogen.

Appendix to Chapter XII.

PROBLEMS.

79. What is the weight of a litre of cyanogen?

80. What volume of air is needed for the combustion of a litre of cyanogen? What volume of each product is formed?

81. What weight of ammonia could be obtained from 1 gramme of urea, supposing the whole of the nitrogen converted into ammonia?

82. What weight of urea nitrate could be obtained by saturating 1 gramme of urea with hydric nitrate?

83. If a gramme of argentic fulminate were broken up into metallic silver, carbonic oxide, and nitrogen, what volume of each of the gases would you obtain?

84. What weight of hydric cyanide is obtained by distilling 500 grammes of crystallized 'ferro-cyanide' ($(CN)_6FeK_4(H_2O)_3$) with dilute hydric sulphate?

85. What is the volume of 10 grammes of methylia? What volume of oxygen is needed for their combustion? What volume of each product is formed?

CHAPTER XIII.

81. Atoms. Each element consists of small indivisible particles called atoms. The elementary atoms are capable of uniting with one another, forming compounds, but they cannot be destroyed by any known process. Each atom of oxygen has the same weight as any other atom of oxygen, so also with hydrogen, nitrogen, carbon, &c.; in fact all the atoms of one element have the same weight; and chemistry teaches that an atom of oxygen is 16 times as heavy as an atom of hydrogen, and this is meant when we say that 16 is the atomic weight of oxygen. An atom of nitrogen is 14 times as heavy as an atom of hydrogen, so that the atomic weight of nitrogen is 14; and an atom of carbon is 12 times as heavy as an atom of hydrogen, so that the atomic weight of carbon is 12. In like manner the atomic weight of each of the other elements tells us the weight of every atom of that element, taking the weight of the atom of hydrogen as *one*.

Each atom has different properties under different circumstances: its own weight is, however, a property which each atom retains under all circumstances. Thus the volume or tension of oxygen increases with rise of temperature, and the velocity with which its atoms diffuse through an opening in a vessel increases also. With some substances, such as mercury, oxygen does not combine at the ordinary temperature; but at a higher temperature the oxygen is converted by contact with mercury into a solid red powder which contains the

atom of mercury united with the atom of oxygen in couples (Hg O). The atoms of mercury are in as solid a state as those of a solid bar of the metal frozen by carbonic acid; and the atoms of oxygen, which no combination of cold and pressure has yet been sufficient to reduce even to the liquid state, are in the mercuric oxide perfectly solid.

82. Nearly all atoms require about the same amount of heat to raise their temperature one degree; thus 108 grms. of silver absorb the same amount of heat in being heated one degree, as 7 grms. of lithium or 23 grms. of sodium. The following table shows the amount required to raise a weight of the element in the solid condition, proportional to its atomic weight, through one degree.

	Atomic heat.		Atomic heat.
Lithium	6.59	Antimony	6.19
Sodium	6.75	Iodine	6.87
Magnesium	6.00	Gold	6.36
Aluminium	5.89	Platinum	6.42
Phosphorus (solid)	5.85	Mercury (solid)	6.38
Sulphur	5.68	„ (liquid)	6.66
Potassium	6.61	Thallium	6.84
Manganese	6.69	Lead	6.5
Iron	6.37	Bismuth	6.48
Nickel	6.5	Boron (graphitic)	2.59
Cobalt	6.3	„ (crystallized)	2.75
Copper	6.04	Carbon (wood charcoal)	2.9
Zinc	6.21	„ (graphite)	2.41
Arsenic	6.11	„ (diamond)	1.76
Bromine (solid)	6.75	Silicon (crystallized)	4.97
Silver	6.16	„ (fused)	4.9
Tin	6.63		

These numbers are obtained by multiplying the atomic weight of each element into its specific heat, and it will be noticed that the mean, except in the case of boron, carbon, and silicon, is about 6.4. These numbers are termed the **atomic heats** of the elements, because they express the amount of heat required to raise the temperature of each atom through one degree. The atomic heats of the gases,

oxygen, hydrogen, and nitrogen, average 3.4, and of chlorine and bromine vapour, 4.3.

83. Molecule is the name given to the smallest cluster of atoms of any substance, whether an element or a compound, that is believed capable of existing by itself, and every pure compound consists of similar molecules.

The following formulæ represent the molecules of the gaseous substances which have been described in the preceding pages, and each formula taken in grammes represents 22.4 litres, or 2 volumes of the respective gas, and may be called the 'absolute molecule':—

Oxygen, O^2,	Ammonia, NH_3.
Hydrogen, H^2.	Marsh gas, CH_4.
Nitrogen, N^2.	Ethylene, C^2H_4.
Steam, H_2O.	Acetylene, C^2H_2.
Nitrous oxide, N_2O.	Butylene, C^4H_8.
Nitric oxide, NO.	Cyanogen, C^2N_2.
Nitric peroxide, NO_2.	Prussic acid, CNH.
Carbonic oxide, CO.	Formiate, CH_2O_2.
Carbonic acid, CO_2.	

None of these absolute molecules (containing hydrogen) has got less than 1 gramme of hydrogen. Some contain 2, 3, or 4 grammes of it, but no molecule has got a fraction of an atom of hydrogen.

So also with regard to oxygen, some of our absolute molecules contain 16 grammes of oxygen, others contain entire multiples of 16 grammes of oxygen.

Nitrogen in like manner combines in the proportion of 14 grammes in one molecule and entire multiples of that number, and carbon in the proportion of 12 grammes and multiples of 12 grammes. None of these molecules contains a fraction of any atomic weight.

Thus it is that the study of the constitution of gaseous molecules proves the truth of the atomic theory.

There are, however, many compounds which cannot be obtained in the state of vapour, and of any such compound

the formula which represents the smallest cluster which can be shewn (by an accurate comparison of the various reactions of the compound) to exist by itself is the formula of the molecule.

Hydric oxalate ($C^2O_4H_2$) might, consistently with the atomic weights of its elements, be represented by the formula CO_2H, but the study of the oxalates has shewn that CO_2H does not exist by itself, and that $C^2O_4H_2$ is the smallest group of the oxalate which can take part in any reaction; for we can take out one atom of hydrogen and put in one atom of potassium in its place, forming the hydro-potassic oxalate C^2O_4HK; or we can replace both atoms of hydrogen by potassium in a similar manner, forming the neutral potassic oxalate $C^2O_4K_2$. The molecule of ammonia is represented by the formula NH_3; for one-third of the hydrogen can be taken out and replaced by an atom of another kind, or two-thirds of the hydrogen can be taken out and replaced, or, finally, the whole of the hydrogen can be replaced by three atoms of some other element.

The **molecular weight of a hydrogen salt** is that weight which contains as many atoms of hydrogen replaceable by potassium or silver as have been separately replaced by such a metal. Hydric oxalate and carbonate have the molecular formulæ $C^2O_4H_2$ and CO_3H_2, because potassium can replace either one or both atoms of hydrogen in these weights of the compound. Nitrate and chlorate have the molecular formulæ NO_3H and ClO_3H, because potassium never replaces part of the hydrogen in one of the acids, so as to form a compound derivable from any multiple of these formulæ, having part of the hydrogen replaced by potassium. There is no hydro-potassic nitrate or hydro-potassic chlorate with such a formula as N_2O_6HK, or $N_3O_9H_2K$, or $N_3O_9HK_2$, &c.

84. The term 'atom' was explained above only in its

application to elements. It is, however, applied to compounds, in accordance with the same principles which regulate its application to elements. Whenever a group of elements forms a compound corresponding to one formed by an element, or in fact, whenever a group behaves like an element, such group of elements is called a **radical**, and the term 'atom' is applied to radicals exactly in the same way as it is applied to elements. Thus NH_4 is a radical analogous to potassium, and NH_4 is capable in many compounds of taking the place of K. NH_4 is called an atom of ammonium.

So also CN combines in a similar manner to Cl, and is a radical comparable to the element chlorine. CN is called an atom of cyanogen. But neither NH_4 nor CN are believed capable of existing by themselves, any more than Cl. If ammonium be ever made, its molecule will doubtless be found to correspond to the formula $(NH_4)^2$, just as the molecule of cyanogen is found to be $(CN)^2$, and the molecule of chlorine Cl^2.

85. The elements oxygen, nitrogen, and carbon form with hydrogen the compounds H_2O, H_3N, H_4C. Each atom of oxygen in water is combined with two atoms of hydrogen, each atom of nitrogen in ammonia is combined with three atoms of hydrogen, and each atom of carbon in marsh gas is combined with four atoms of hydrogen; and these quantities of the three compounds occupy precisely the same volume in the state of vapour, so that a cubic centimetre of ammonia gas has got three atoms of hydrogen in it, for every two atoms of hydrogen in a cubic centimetre of steam; and a cubic centimetre of marsh gas has got four atoms of hydrogen in it for every two atoms of hydrogen in an equal volume of steam, or for every three atoms of hydrogen in the cubic centimetre of ammonia—

$H_2O = 2$ vols, $NH_3 = 2$ vols, $CH_4 = 2$ vols.

There are other elements, such as chlorine, potassium, silver, &c., which resemble hydrogen in the atomic constitution of their compounds with oxygen, nitrogen, and carbon. They form, for instance, the compounds Cl_2O, K_2O, Ag_2O, Cl_3N, K_3N, Ag_3N, Cl_4C, &c., so that one atom of oxygen combines with two atoms of hydrogen, or of these other elements. Nitrogen combines with three atoms of hydrogen, or three of these other elements; and so also the atom of carbon combines with four atoms of elements of the hydrogen class.

When hydrogen combines with chlorine, or any other element of its own class, it is always in the proportion of one atom of each; and the molecule of hydric chloride occupies in the state of vapour the same volume as any other molecule, Cl H = 2 vols.

When chlorine in hydric chloride is replaced by oxygen the process takes place in the following proportions, viz. $H_2Cl_2 + O = H_2O + Cl^2$. One atom of oxygen takes the place of two atoms of chlorine, and it is spoken of as *equivalent to* two atoms of chlorine. It is not necessary for the establishment of this relation between oxygen and chlorine that one atom of oxygen be capable of turning out two atoms of chlorine from hydrochloric acid, for even if no such decomposition were possible we might compare a molecule of water H_2O with that quantity of hydrochloric acid which is equal to it in hydrogen, viz. with two molecules of hydric chloride 2 (H Cl), and we might say that to transform one of the compounds into the other a change of place between two atoms of chlorine and one atom of oxygen would be needed. Oxygen is from this peculiarity called a di-valent element. A similar reasoning shews nitrogen to be tri-valent; and carbon is tetra-valent.

Many of the most important peculiarities of compounds depend upon the value of the elements contained in them.

When marsh gas is burnt, the formula

$$C H_4 + 2 O^2 = C O_2 + 2 H_2 O$$

describes the atomic proportions in which the process takes place. The product $C O_2$ has been formed from $C H_4$ by taking away the four atoms of hydrogen and putting in two atoms of oxygen in their place. And in like manner the other product, $2 H_2 O$, is formed by taking out one atom of carbon from each molecule of marsh gas, and replacing it by two atoms of oxygen. In describing this result it is customary to say that two atoms of oxygen are 'equivalent to' four atoms of hydrogen, and that two atoms of oxygen are 'equivalent to' one atom of carbon. The term 'equivalent' is not intended to convey the idea of any equality of properties.

When prussic acid is burnt, the equation

$$2 C N H + 5 O = 2 C O_2 + N^2 + H_2 O$$

represents the atomic proportions of the process; and the carbonic acid is formed by four di-valent atoms of oxygen taking the place of two tri-valent atoms of nitrogen, and of two mono-valent atoms of hydrogen. The sum of the atomic values of the oxygen going into combination, is equal to the sum of the values of the elements going out of the compound. This relation holds good in all decompositions in which the elements retain their original values.

The value of any atom is equal to the number of atoms of hydrogen or chlorine, or potassium, or silver, with which one atom of element can combine, or the number of such atoms which it can be represented as replacing.

86. When carbon is burnt so as to form carbonic oxide, each molecule of the compound $C O$ contains one tetravalent atom of carbon united with one di-valent atom of oxygen, and in carbonic oxide one of the two atoms has accordingly a value different from usual. We might say

that the carbon is di-valent in carbonic oxide, or else that oxygen is tetra-valent.

When carbonic oxide is burned forming CO_2, both the elements have their usual value, and we must admit that one of them underwent a change of value during the combustion.

When olefiant gas is completely burnt the reaction is $C^2H_4 + 3O^2 = 2CO_2 + 2H_2O$. The four mono-valent atoms of hydrogen in the olefiant gas are here replaced by four di-valent atoms of oxygen, and the apparent value of the carbon is doubled.

If four atoms of oxygen only were supplied to each molecule of olefiant gas, and half of it combined with the hydrogen, while the other half combined with the carbon, forming carbonic oxide,—$C^2H_4 + 2O^2 = 2CO + 2H_2O$,—the four mono-valent atoms of hydrogen would be replaced by two di-valent atoms of oxygen, and the carbon would continue apparently di-valent.

Atoms of Uneven Value.

Monads.		Triads.	
Hydrogen	H ≧ 1	Nitrogen	N = 14
Fluorine	F = 19	Phosphorus	P = 31
Chlorine	Cl = 35·5	Arsenic	As = 75
Bromine	Br = 80	Antimony	Sb = 122
Iodine	I = 127	Bismuth	Bi = 210
Lithium	Li = 7	Boron	B = 11
Sodium	Na = 23	Gold	Au = 196
Potassium	K = 39	Vanadium	V = 51·3
Rubidium	Rb = 85	Indium	In = 113·5
Cœsium	Cs = 133		
Thallium	Tl = 203		
Silver	Ag = 108		

Atoms of Even Value.

Dyads, Tetrads, &c.

Oxygen	O	=	16
Sulphur	S	=	32
Selenium	Se	=	79.5
Tellurium	Te	=	129
Calcium	Ca	=	40
Strontium	Sr	=	87.5
Barium	Ba	=	137
Lead	Pb	=	207
Mercury	Hg	=	200
Magnesium	Mg	=	24
Zinc	Zn	=	65
Cadmium	Cd	=	112
Aluminium	Al	=	27.5
Iron	Fe	=	56
Chromium	Cr	=	52.5
Manganese	Mn	=	55
Cobalt	Co	=	58.5
Nickel	Ni	=	58.5
Copper	Cu	=	63.5
Glucinum	G	=	9
Yttrium	Y	=	64
Cerium	Ce	=	92
Lanthanium	La	=	92
Didymium	Di	=	96
Uranium	U	=	120
Zirconium	Zr	=	89.5
Tantalum	Ta	=	138
Niobium	Nb	=	195
Thorinum	Th	=	238
Carbon	C	=	12
Silicon	Si	=	28
Tin	Sn	=	118
Titanium	Ti	=	50
Molybdenum	Mo	=	96
Tungsten	W	=	184
Platinum	Pt	=	197
Iridium	Ir	=	197
Osmium	Os	=	199
Rhodium	Ro	=	104
Ruthenium	Ru	=	104
Palladium	Pd	=	106.5

CHAPTER XIV.

87. Chlorine ($Cl^2 = 2$ vols.) is most conveniently prepared by heating finely-powdered manganic peroxide with strong hydric chloride. The manganese seems at first to dissolve as perchloride ($Mn\,Cl_4$), but chlorine gas speedily comes off, leaving manganous chloride—

$$Mn\,O_2 + 4\,(H\,Cl) = Mn\,Cl_2 + Cl^2 + 2\,(H_2\,O).$$

When the mixture is heated in a closed tube, similar to that described for the preparation of liquid ammonia, **liquid chlorine** is obtained. At 15.5° it requires a pressure of four atmospheres for its liquefaction.

At the ordinary atmospheric pressure chlorine is a yellow gas, about two and a half times as heavy as air. Its density is 35.5. At 15°C water dissolves about twice its volume of chlorine gas, and for this reason it is customary to collect the gas by displacement of air. It forms a crystalline hydrate of the composition $Cl\,(H_2\,O)_5$.

The gas has a most suffocating odour, and even two or three per cent. of it renders air quite irrespirable, as it disorganizes the tissues of the air-passages of the lungs.

Chlorine combines with metals, and its compounds are called chlorides. Powdered metallic antimony showered into the gas catches fire. Finely-divided metallic iron also burns in chlorine. In the dry state chlorine does not affect the colour of litmus-paper, but a drop of water thrown on the paper causes the immediate destruction of the colour by chlorine. Some colouring matters are bleached by chlorine

alone, but the greater number of bleaching effects produced by it are with the co-operation of water.

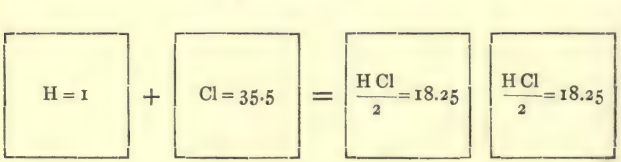
When passed with steam through a red-hot tube, chlorine combines with hydrogen, and liberates oxygen from a portion of the steam.

When passed into a solution of ammonia it gives off nitrogen gas by taking hydrogen from the ammonia. But when passed into a solution of sal-ammoniac, chlorine forms oily drops of nitric chloride, which fall to the bottom of the liquid and detonate with great violence on very slight provocation.

A solution of caustic potash absorbs chlorine, the first product being potassic chloride and a salt of potash with hypochlorous acid—

$$Cl^2 + 2\,(K\,H\,O) = Cl\,K + Cl\,K\,O + H_2\,O.$$

88. Hydric Chloride (H Cl = 2 vols.), frequently called muriatic acid, is formed when a mixture of equal volumes of chlorine and hydrogen is exposed to the sunshine; the mixture explodes, forming gaseous hydric chloride of the same



volume as the mixture. The elements are not known to combine in any other proportion. On a small scale the gas is most conveniently made by heating strong hydric sulphate with lumps of table salt, of the size of hazel nuts, obtained by melting the salt in an earthen crucible, and pouring it out to cool on a stone, then breaking up the cake into fragments of the size described. Half of the hydrogen of the sulphate is replaced by the sodium of the salt, forming hydro-sodic sul-

phate, and the hydrogen which leaves the sulphate goes away in combination with chlorine from the salt. Thus,

$$H_2SO_4 + NaCl = NaHSO_4 + HCl.$$

For manufacturing purposes a similar operation is performed with only half the proportion of sulphate, aided by much stronger heat. The first part of the process then takes place as above, but the hydro-sodic sulphate subsequently reacts on a molecule of salt, forming neutral sodic sulphate and hydric chloride—

$$HNaSO_4 + NaCl = Na_2SO_4 + HCl.$$

The density of the gas is 18.25. At 10°C a pressure of 40 atmospheres is required to liquefy it. Hydric chloride forms dense fumes when allowed to escape into moist air. It dissolves in water with great facility, causing a considerable rise in the temperature of the liquid, and forming a solution of greater density than water. When containing about 40 per cent. of acid, the solution has a density of 1.2. Strong solutions give off gaseous hydric chloride when heated, and they boil constantly at 110°C. Weak solutions give off water, with but little chloride, until their boiling-point has risen to 110°C at the ordinary atmospheric pressure. At this temperature the solution distils uniformly, and contains about 20 per cent. of chloride. Roscoe finds that if the solution be distilled under a pressure of 2 atmospheres, it distils over undecomposed when containing 19 per cent. of acid; and at a pressure of 3 atmospheres it distils regularly only when containing about 18.3 per cent. HCl.

89. Hydric chloride is an exceedingly acid salt, and by double decomposition with potassic hydrate, forms potassic chloride and water, both neutral bodies. There is only one proportion in which the hydrogen of hydric chloride can be removed, in whatever proportions the acid salt may be mixed with the basic compound. The process is this:

$$HCl + HKO = KCl + H_2O.$$

A chloride can be detected in any solution by the characteristic white curdy precipitate which it forms with argentic nitrate. The precipitate, which consists of argentic chloride, is insoluble in hydric nitrate, even on boiling, but dissolves readily in ammonia. Mercurous nitrate is also decomposed by soluble chlorides, forming a precipitate of mercurous chloride, generally known by the name of calomel—

$$(N O_3)_2 Hg^2 + 2 (H Cl) = 2 H N O_3 + Hg^2 Cl_2.$$

One of the most characteristic properties of chlorides is that of yielding a volatile compound with chromium and oxygen, called **chlorochromic acid.** The compound is easily obtained by evaporating a chloride to dryness (having previously added potash if the solution was acid), and mixing the dry residue with potassic dichromate and plenty of strong sulphuric acid, and distilling the mixture in a retort, when a deep-red vapour having the composition $Cr O^2 Cl_2$ goes over into the receiver.

Strong hydric and other chlorides are oxidized by strong hydric nitrate, chlorine and oxides of nitrogen being evolved. The mixture is called aqua regia, from its property of dissolving gold or platinum, metals which are not attacked by either the nitrate or chloride alone.

Commercial hydric chloride is very liable to contain arsenic, and not unfrequently sulphurous acid.

90. Chlorine forms four acid compounds with hydrogen and oxygen, and salts corresponding to them. They are called perchlorates (such as $Cl O_4 H$), chlorates (such as $Cl O_3 H$), chlorites (such as $Cl O_2 H$), and hypochlorites (such as $Cl O H$). Anhydrous acids corresponding to two of these are known, viz. chlorous acid ($Cl_2 O^3$), and hypochlorous acid ($Cl_2 O$). There is also a neutral peroxide, $Cl_2 O^4 = 4$ vols. Hydric perchlorate ($H Cl O_4$) can be obtained by decomposing a solution of potassic perchlorate by

hydrofluosilicic acid. The potassium is carried down as fluosilicate, while hydric perchlorate is formed—

$$Si\,Fl_6\,H_2 + 2\,(Cl\,O^4\,K) = Si\,Fl_6\,K_2 + 2\,(Cl\,O^4\,H).$$

When obtained as a monohydrate, the **perchlorate** is a liquid of 1.78 density at 15.5° (Roscoe). In contact with charcoal it explodes with great violence. The acid forms a crystalline hydrate, $Cl\,O^4\,H\,H_2\,O$. Dilute solutions of the perchlorate dissolve zinc with evolution of hydrogen, and formation of zinc perchlorate. Hydric chlorate is best prepared by adding dilute hydric sulphate to a solution of baric chlorate, in quantity exactly sufficient to remove all the barium, without leaving any sulphate mixed with the chlorate. Baric sulphate is completely precipitated—

$$Ba\,(Cl\,O^3)_2 + S\,O_4\,H_2 = 2\,(Cl\,O^3\,H) + S\,O_4\,Ba.$$

The solution of the **chlorate** may be concentrated by evaporation at a gentle heat; but the process should be completed by putting the partially concentrated acid hydrogen salt into a vacuum beside some oil of vitriol. The chlorate, when containing but a little free water, is decomposed by light, and becomes yellow, owing to the formation of chlorous acid. It is decomposed by distillation, perchlorate being formed, besides other products. A piece of blue litmus-paper is reddened by strong chlorate, but a bleaching action immediately follows. Chlorates are powerful oxidizing agents, and present many points of analogy with nitrates. They are monobasic, and are remarkable for their solubility. Even the argentic, plumbic, and baric chlorates are soluble in water.

Strong hydric sulphate decomposes a chlorate, with evolution of a deep yellow gas, which explodes when gently heated. Oxygen is given off at the same time, and the yellow gas called **chloric peroxide** appears to have the composition $Cl_2\,O^4 = 4$ vols.

90 *a*. **Chlorous Acid** is obtained by the partial desoxidation

of chloric acid. It is a weaker acid than chloric acid, but presents in other respects great resemblance to it.

Hypochlorites. The hydrogen salt (Cl O H) is obtained by shaking up chlorine water with mercuric oxide. Its solution in water is colourless, and has a peculiar sickly odour. It is an exceedingly weak acid hydrogen salt, being expelled by carbonic acid from its salts in presence of water. It is an exceedingly powerful bleaching agent, and is present together with hydric chloride in the solution of chlorine in water. There is no difficulty in removing the chloride from the solution, by adding to it a solution of argentic nitrate as long as any precipitate is formed. The decomposition is thus represented—

$$Cl^2 + H_2O + N O_3 Ag = Cl Ag + Cl O H + N O_3 H.$$

After the action of the nitrate has removed half the chlorine the solution retains all the bleaching power which it had before the silver salt was added. When a concentrated solution of a hypochlorite is mixed with concentrated hydric chloride, an action takes place in the reverse direction to that of chlorine on water—

$$Cl H + Cl O H = Cl^2 + H_2O.$$

Hypochlorous Acid ($Cl_2O = 2$ vols.) is obtained in the form of a yellow gas by passing chlorine over red mercuric oxide, both substances being dry.

The compound so much used by the name of bleaching powder is a mixture of calcic hypochlorite with calcic oxychloride. The hypochlorite can be liberated by adding dilute sulphate, little by little, to bleaching powder mixed with water, and agitating the mass whilst the sulphate is running into it. In this manner the weak hypochlorite is alone decomposed and hydric hypochlorite can be distilled over. If too much sulphuric acid were to be added, hydric chloride would also be evolved from the calcic chloride, and by acting on the hypochlorite would evolve chlorine.

91. Nitric Chloride (NCl_3) is obtained by passing chlorine into a solution of sal-ammoniac. It gradually goes to the bottom of the liquid, and is most safely collected in a hollow block of lead. A great number of organic bodies possess the property of causing this compound to explode, and the violence with which it explodes is so great as to shatter any glass or earthenware vessel.

The products of the decomposition are free nitrogen and chlorine.

Chloronitrous Acid (NOCl = 2 vols.) is one of the substances formed by the action of hydric nitrate on hydric chloride. It can be condensed by a frigorific mixture from the vapours given off by aqua regia. Nitric oxide combines directly with chlorine, forming this compound.

92. Ammonic Chloride (NH_4Cl = 4 vols.). This salt is commonly called sal-ammoniac, and sometimes muriate of ammonia.

It is usually made in this country by adding hydric chloride to the so-called gas-liquor, which is an impure solution of ammonia, containing carbonic acid, sulphuretted hydrogen, and other weak acids. The crude salt is purified by crystallization, by heating the crystals, and finally by sublimation. It is very soluble in water, and by evaporation of its solution the salt can be obtained in cubical, or sometimes in octohedral, crystals. When heated by itself it evaporates, and the vapour formed by the evaporation of one molecule of the salt occupies the sum of the volumes occupied by free ammonia and by free hydric chloride d from this circumstance it is concluded that the salt is decomposed by evaporation into free hydric chloride and free ammonia, just as mercuric oxide is decomposed by heat into free mercury and oxygen.

Ammonic chloride is formed by adding a solution of ammonic carbonate to a solution of calcic chloride; calcic

carbonate being precipitated, while the ammonic chloride remains in solution—

$$Ca\,Cl_2 + (N\,H_4)_2\,C\,O_3 = C\,O_3\,Ca + 2\,(N\,H_4\,Cl);$$

but if the mixture of calcic carbonate and sal-ammoniac be boiled, the reverse process takes place, ammonic carbonate being carried away by the steam as fast as it is formed, while calcic chloride remains in the solution.

Iron exposed to the air becomes rusty very rapidly when moistened with a solution of sal-ammoniac.

93. Chlorocarbonic Acid ($C\,O\,Cl_2 = 2$ vols.) is frequently called phosgene gas.

The most easy way of obtaining this gas is to pass a mixture of equal volumes of chlorine and carbonic oxide through a long glass tube exposed to bright sunshine. The mixture condenses into half its volume of a colourless gas, consisting of chloro-carbonic acid, possessing a most suffocating odour. Its density is 49.5.

$$\frac{CO}{2} = 14 \quad + \quad Cl = 35.5 \quad = \quad \frac{COCl_2}{2} = 49.5$$

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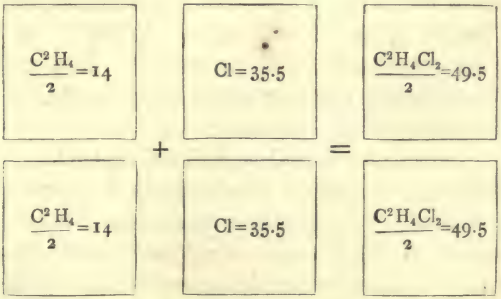
The gas may be considered as carbonic acid, in which one atom ofo xygen is replaced by an equivalent quantity, namely, two atoms of chlorine. In contact with moisture it is rapidly decomposed, with formation of hydric chloride and carbonic acid; $C\,O\,Cl_2 + H_2O = C\,O_2 + 2\,(H\,Cl)$.

With dry ammonia phosgene forms a compound of ami-

dogen ($N H_2$) with carbonic oxide, called urea, together with ammonic chloride—

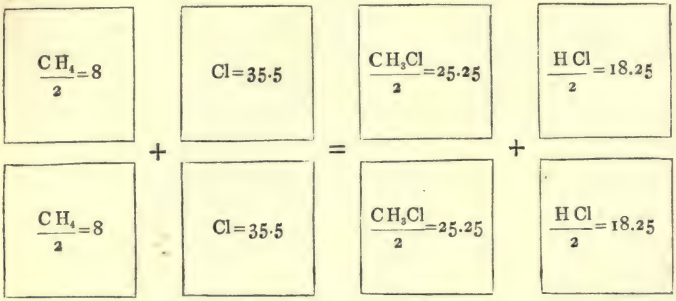
$$4 (N H_3) + C O Cl_2 = C O (N H_2)_2 + 2 (N H_4 Cl).$$

94. The **action of chlorine** on compounds of carbon and hydrogen is of two kinds. With some hydrocarbons it combines in the proportion of two atoms of chlorine to one molecule of the hydrocarbon. Olefiant gas affords an instance of this action, for when equal volumes of chlorine and olefiant gas are mixed in presence of water, the gases combine, forming a heavy oily liquid of the composition $C^2 H_4 Cl_2 = 2$ vols. This substance has obtained the name "**Dutch liquid.**" It is not dissolved or acted upon by water, nor by a solution of potash in water. It boils without decomposition at about 84°C, and its vapour has a sweetish and agreeable odour not unlike that of chloroform. The liquid has a density of 1.28 at 0°C, and its vapour has a density of 49.5.



The other kind of action of chlorine on hydrocarbons is illustrated by the case of marsh gas. The two atoms of chlorine react on one molecule of that hydrocarbon, but one of these atoms of chlorine takes hydrogen out of the hydrocarbon, forming hydric chloride, while the other atom of chlorine takes the place of the atom of hydrogen in the hydrocarbon. Thus, a mixture of two volumes of chlorine

with two volumes of marsh gas forms two volumes of hydric chloride, and a compound of CH_3 with one atom of chlorine; $CH^4 + Cl^2 = CH^3Cl + HCl$.



The compound CH_3Cl is called **methylic chloride.** It dissolves in water at the temperature of 14°, to the extent of several times the volume of the water; and at temperatures below 6°C it forms a crystalline compound with water. When heated to 100°C with potassic hydrate it is decomposed, the potassium combining with its chlorine, and the group CH_3, called **methyl**, taking the place of the potassium, forming methylic hydrate—

$$CH_3Cl + KHO = KCl + CH_3HO.$$

Methylic chloride can be condensed to the liquid state by the aid of a powerful frigorific mixture, and boils at −23.73.

A mixture of equal volumes of chlorine and methylic chloride is in its turn decomposed by sunshine, the action of the chlorine being an exact repetition of the process by which the chloride itself was formed: viz.

$$CH_3Cl + Cl^2 = CH_2Cl_2 + HCl.$$

This body is an oil, insoluble in water, having a density of 1.344 at 18°C, and a boiling-point of 30.5. Its vapour has the same volume as that of methylic chloride—

$$CH_2Cl_2 = 2 \text{ vols.};$$

so that the atom of chlorine has taken the place of one atom of hydrogen in methylic chloride, without disturbing the other atoms of the compound.

By repeating the action of chlorine, a still further substitution of hydrogen by chlorine can be effected in a precisely similar manner ($C H_2 Cl_2 + Cl^2 = C H Cl_3 + H Cl$), and the compound thus obtained is the well-known

95. Chloroform ($C H Cl_3 = 2$ vols.). This compound is prepared on a large scale by distilling spirits of wine with bleaching powder mixed with a large quantity of water. It is heavier than the compound $C H_2 Cl_2$, and has a higher boiling-point, its density being 1.491 at 17°C, and its boiling-point 60.16°C. It is not acted upon by water under 100°C, nor can its chlorine be discovered by an aqueous solution of argentic nitrate. It is, however, dissolved by alcohol, and potash can then be mixed with it, when on the application of heat a brisk decomposition takes place, potassic chloride and formiate being formed—

$$C H Cl_3 + 4 (K H O) = K C H O_2 + 3 (K Cl) + 2 (H_2 O).$$

Chloroform is much used for allaying temporarily the sensation of pain, an action which is termed **anæsthetic**. When inhaled in sufficient quantity with air, it entirely suspends the consciousness of the patient.

Its vapour is decomposed by passing through a red-hot tube, and if moisture is present hydric chloride is thus obtained in abundance.

96. Carbonic Chloride ($C Cl_4 = 2$ vols.). By passing the vapour of chloroform with an excess of chlorine through a red-hot glass tube this compound is formed. Its density is 1.599, and it boils at 76.05. When potassium-amalgam is put into a solution of carbonic chloride in alcohol, the chlorine is gradually taken out of it, and replaced atom for atom by hydrogen. In this manner marsh gas can be recovered from the chloride.

The intermediate compounds $C\,H\,Cl_3$, $C\,H_2\,Cl_2$, and $C\,H_3\,Cl$ are, however, formed at the same time, and the process must be considered as a substitution of one atom of chlorine at a time by hydrogen. Thus—

$$C\,Cl_4 + H^2 = C\,H\,Cl_3 + H\,Cl,$$
$$C\,H\,Cl_3 + H^2 = C\,H_2\,Cl_2 + H\,Cl, \text{ \&c.}$$

The hydrogen must for this purpose be in the nascent state, as free hydrogen does not produce the effect.

There is also a chloride of carbon ($C^2\,Cl_4$) corresponding to olefiant gas, a liquid which boils at 122°C, and another formed from it at high temperatures corresponding to acetylene and having the formula $C^2\,Cl_2$. This protochloride is a crystalline solid which evaporates without fusion at 200°C.

Cyanogen forms three polymeric compounds with chlorine —a gaseous, a liquid, and also a solid, chloride. They are obtained by the action of chlorine on prussic acid or mercuric cyanide; $C\,N\,H + Cl^2 = C\,N\,Cl + H\,Cl$.

The solid chloride corresponds to cyanuric acid, and consists of three molecules of the gaseous chloride united in one, $C^3\,N^3\,Cl^3$[m].

m Examples of chlorides and double chlorides:—

Hydric chloride, $H\,Cl$.
Potassic chloride, $K\,Cl$.
Argentic chloride, $Ag\,Cl$.
Stannous chloride, $Sn\,Cl_2$.
Calcic chloride, $Ca\,Cl_2$.
Zinc chloride, $Zn\,Cl_2$.
Cupric chloride, $Cu\,Cl_2$.
Cuprous chloride, $Cu^2\,Cl_2$.
Mercuric chloride, $Hg\,Cl_2$.
Mercurous chloride, $Hg^2\,Cl_2$.
Antimonious chloride, $Sb\,Cl_3$.
Boric chloride, $B\,Cl_3$.
Auric chloride, $Au\,Cl_3$.
Potassio-mercuric chloride, $K\,Hg\,Cl_3$.
Potassio-magnesic chloride, $K\,Mg\,Cl_3$.
Carbonic chloride, $C\,Cl_4$.
Stannic chloride, $Sn\,Cl_4$.
Platinic chloride, $Pt\,Cl_4$.
Hyd-auric chloride, $H\,Au\,Cl_4$.
Sod-auric chloride, $Na\,Au\,Cl_4$.
Potassio-mercuric chloride, $K_2\,Hg\,Cl_4$.
Potassio-cupric chloride, $K_2\,Cu\,Cl_4$.
Ferric chloride, $Fe^2\,Cl_6$.
Aluminic chloride, $Al^2\,Cl_6$.
Hydro-platinic chloride, $H_2\,Pt\,Cl_6$.
Potassio-platinic chloride, $K_2\,Pt\,Cl_6$.
Ammonio-platinic chloride, $(N\,H_4)_2\,Pt\,Cl_6$.
Bari-platinic chloride, $Ba\,Pt\,Cl_6$.
Potassio-stannic chloride, $K_2\,Sn\,Cl_6$.

Appendix to Chapter XIV.

PROBLEMS.

86. What volume of hydrogen would be obtained by passing a litre of hydric chloride gas over hot metallic iron?

87. What weight of common salt would be needed for the preparation of a kilogramme of hydric chloride? What volume will the gas occupy?

88. What weight of pure "manganese" is needed for the evolution of 100 grammes of chlorine?

89. A litre of chlorine is passed with an excess of steam through a red-hot porcelain tube. What volume of oxygen is liberated, assuming that all the chlorine combines with hydrogen?

90. What weight of potassic hydrate is needed for the neutralization of 100 grammes of gaseous hydric chloride?

91. What volume of ammonia gas is required for the neutralization of 10 grammes of gaseous hydric chloride?

92. 20 grammes of an aqueous solution of hydric chloride were mixed with an excess of argentic nitrate. The precipitate (argentic chloride) was collected, washed, dried, and weighed. It amounted to 4.53 grammes. Calculate the percentage of hydric chloride in the original solution.

93. What is the weight of a litre of sal-ammoniac vapour, reduced to the normal temperature and pressure?

94. A litre of phosgene gas is completely decomposed into carbonic acid and hydric chloride by the action of water. What is the volume of each product?

95. What volume of chlorine can be made to combine

directly with a litre of olefiant gas? What is the vapour-volume of the product?

96. What is the weight of a litre of chloroform vapour?

97. Suppose a litre of carbonic chloride to be decomposed by water according to the formula

$$C Cl_4 + 2 (H_2O) = C O_2 + 4 (H Cl),$$

what volume of each product would be formed?

CHAPTER XV.

97. Bromine (Br = 80; Br^2 = 2 vols.) is found in the mother liquor of sea-water in combination with sodium and potassium, and can be set free from those compounds by the action of chlorine. On a larger scale it is prepared by processes similar to those adopted for the preparation of chlorine. Bromine is a dark-red liquid of 2.966 density. It dissolves slightly in water, and the solution has the powerful odour of bromine, an odour which is even more distressing to the respiratory organs than chlorine itself. Bromine boils at 47°, and evaporates very freely at ordinary temperatures. Its vapour has a deep-red colour, not unlike that of nitric peroxide. The vapour of bromine has a density equal to 80.

In its compounds bromine exhibits great analogy with chlorine, but is decidedly less energetic in its action. Thus a mixture of equal volumes of bromine vapour and hydrogen cannot be made to combine with explosion; and hydric bromide once formed by indirect means is more easily decomposed than the chloride. In proof of this it is sufficient to heat potassic bromide with strong hydric sulphate, so as to evolve the bromide in contact with hot sulphate. There is an immediate action between these two acids, liberating bromine, by decomposition of some of the bromide: thus,

$$H_2SO_4 + 2(HBr) = SO_2 + Br^2 + 2(H_2O).$$

98. Hydric bromide (Br H = 2 vols.) is most conveniently prepared by the action of water upon phosphoric bromide;

$$P Br_5 + 4 (H_2 O) = P O_4 H_3 + 5 (H Br).$$

The aqueous solution of the acid salt has much resemblance to the chloride, and by double decomposition with bases it forms metallic bromides analogous to the corresponding chlorides. **Argentic bromide** has much resemblance to the chloride. It is however less soluble in ammonia, so that when potassic bromide is added to ammonia saturated by argentic chloride, a precipitate of argentic bromide is obtained.

Bromine does not, like chlorine, form a volatile compound with chromium and oxygen, so that when a bromide is distilled with potassic di-chromate and hydric sulphate, bromine vapour escapes, without carrying over any chromium.

Bromates, such as hydric-bromate ($Br O_3 H$), can be obtained by processes similar to those employed for the preparation of chlorates. The silver bromate is insoluble in water. Hypobromites such as Br O H are very much like hypochlorites. The hydrogen salt is readily obtained by agitating bromine water with red mercuric oxide.

By the action of bromine upon hydric perchlorate the perbromate ($H Br O_4$) is formed.

The action of bromine on hydrocarbons is of the same kind as that of chlorine. The compound of bromine with olefiant gas ($C^2 H_4 Br_2$) is an oil of 2.16 density and 132°C boiling-point. It crystallizes easily. The chloride was described above as having a density of 1.28 and the boiling-point 84°; and whenever chlorine and bromine form similar liquid and volatile compounds the bromide is heavier and has a higher boiling-point than the chloride.

99. Iodine (I = 127; I^2 = 2 vols.) is found chiefly in the mother liquor from kelp (the ashes of sea-weeds) in combination with the alkali metals. The method of extraction is very

similar to that employed in the case of bromine, but the iodine which is liberated condenses easily into shining black scales of 4.95 sp. gr.

Iodine is precipitated as a black powder by the action of chlorine or of bromine on a solution of an iodide, being very slightly soluble in water. The most convenient way of recovering for use iodine which has been combined with metals is by the action of hydric nitrite, such as is obtained by the reduction of the nitrate in the cells of a galvanic battery.

Iodine melts at 107°C and boils at 175°C. Its vapour has a beautiful violet colour, and a density of 127. It dissolves in alcohol with a red colour, and also in a solution of potassic iodide, but its solution in carbonic sulphide has a violet colour. Free iodine forms with starch a deep blue compound, by which even the minutest traces of the element can be detected.

100. Hydric Iodide (I H = 2 vols.) is formed in small quantities by passing hydrogen and iodine through a red-hot tube. The best way to obtain the iodide for use is by decomposing a mixture of iodine and phosphorous iodide by water. An aqueous solution of the iodide is easily made by passing sulphuretted hydrogen through water in which iodine is suspended. The solution cannot be kept in contact with air without undergoing decomposition, and becoming red from the presence of free iodine dissolved in it. It is also decomposed by many compounds of oxygen (such as the nitrite), in which that element is feebly combined. It is even more readily decomposed than the bromide by oil of vitriol. The precipitate which it forms with argentic nitrate is insoluble in ammonia. When added to a solution of mercuric chloride it forms a brilliant scarlet precipitate of mercuric iodide. With soluble salts of lead it forms a yellow precipitate of plumbic iodide, which crystallizes from hot water in beautiful scales. A solution of palladic nitrate forms with an iodide a black precipitate of palladic iodide. This reaction affords

the best separation of iodine from bromine, as bromine forms a soluble salt with palladium.

101. The compounds of iodine with most elements have considerable analogy with those of bromine and chlorine; but there are several elements which are unable to combine with as great a number of atoms of iodine as of bromine or chlorine. Thus phosphorus forms a penta-chloride and a penta-bromide, but no penta-iodide, and no very distinct compound beyond the biniodide (P^2I_4). Iron and copper form respectively the compounds Fe^2Cl_6 and $CuCl_2$, but the corresponding iodides decompose immediately into free iodine and a lower salt, in the one case ferrous and in the other cuprous iodide.

102. Two oxygen acids of iodine are known, namely, iodic acid, forming iodates such as the hydrogen salt HIO^3, and periodic acid, forming periodates, such as

$$HIO^4 \text{ or } Na_2HIO^5.$$

Iodic Acid (I_2O^5) is obtained by boiling iodine with hydric nitrate. It crystallizes readily from a concentrated aqueous solution. Potassic iodate is formed by fusing potassic iodide with potassic chlorate.

The argentic and baric iodates are insol ble in water.

Iodic acid is broken up by heat into free iodine and oxygen.

A **Periodate** can be formed by the simultaneous action of sodic iodate and chlorine on a solution of sodic hydrate. The hydrogen salt is liberated from plumbic periodate by hydric sulphate. The hydro-disodic periodate (IO^5Na_2H) is almost insoluble in water. There is also a more soluble dihydro-sodic periodate (H_2NaIO^5).

103. Nitric Iodide is the name given to a black powder, of varying composition, obtained by the action of iodine on a solution of ammonia. It consists of ammonia of which the hydrogen is partly replaced by iodine, atom for atom, and is remarkable for the sharp detonation with which it is

decomposed, when rubbed or slightly pressed in the dry state. Iodine combines with olefiant gas under the influence of sunshine, forming a crystalline compound ($C^2H_4I_2$) corresponding to Dutch liquid.

104. On hydrocarbons generally iodine has no action, or a very feeble one; but the compounds CHI_3, CH_2I_2, CH_3I, can be obtained by indirect means. The first (iodoform) is obtained by the action of iodine on spirits of wine in presence of potash. It crystallizes in beautiful yellow scales, which decompose when heated by themselves, but can be slowly volatilized by a current of steam. CH_3I is called methylic iodide. It is obtained by the action of phosphorous iodide on the compound CH_4O (methylic alcohol). Methylic iodide is a heavy oil of a rather fragrant odour. Its density is 1.9, and boiling-point 44°C. When dissolved in alcohol it is decomposed by argentic nitrate; thus,

$$CH_3I + NO_3Ag = CH_3NO_3 + IAg.$$

Cyanic Iodide (CNI) is a solid compound, which crystallizes in beautiful needles. It is easily obtained by mixing mercuric cyanide with iodine and applying gentle heat, when mercuric iodide is formed, and cyanic iodide sublimes out—

$$Hg(CN)_2 + 2I^2 = HgI_2 + 2(CNI).$$

Iodine combines with chlorine in two proportions, forming an iodous chloride (ICl), and an iodic chloride (ICl_3). In presence of an abundance of water each atom of iodine reacts upon five atoms of chlorine, forming hydric iodate and iodide.

105. Fluorine (F=19) is not known in the free state. Hydric fluoride decomposes manganic binoxide with evolution of oxygen. Chlorine decomposes argentic fluoride, but if the experiment be performed in a glass vessel the glass is attacked. No compound of fluorine with oxygen is known.

106. Hydric Fluoride (HF) is prepared by distilling pure fluorspar in the state of fine powder, or ammonic

fluoride, with hydric sulphate. The experiment cannot be performed in a glass vessel, as glass is dissolved by the fluoride. A platinum vessel is best suited for the purpose—

$$Ca\,F_2 + S\,O_4\,H_2 = Ca\,S\,O_4 + 2\,(H\,F).$$

The receiver should be surrounded by ice, as the acid is exceedingly volatile. The acid is commonly kept in a dilute state, in bottles made of gutta-percha.

Its most remarkable reaction is that of forming a volatile compound of fluorine and silicon by mere contact with silica, or any silicate, such as glass—

$$Si\,O_2 + 4\,(H\,F) = Si\,F_4 + 2\,(H_2\,O).$$

A glass plate covered by a varnish of bees'-wax and turpentine is not attacked by the acid nor by its vapour, but if the coating be removed in some places, by scratching with a needle, the vapour of the fluoride will engrave the glass along the lines thus exposed.

Hydric fluoride appears to be dibasic, for by double decomposition with potash it forms not only a potassium salt but also a double salt, hydro-potassic fluoride, of considerable stability ($H\,K\,F_2$). With ammonia it forms a similar double salt with great readiness. The element has, moreover, a great resemblance to oxygen in its chemical deportment, for silicic fluoride combines with potassic fluoride, baric fluoride, and other fluorides, forming salts, which may be compared to the salts formed by the union of silica itself with potash, &c.,

$$Si\,F_6\,K_2,\quad Si\,F_6\,Ba,$$

and hydric fluo-silicate,

$$Si\,F_6\,H_2,\ \text{like}\ Si\,O_3\,H_2.$$

Fluorine forms with many other elements besides silicon compounds of acid properties; among them is boric fluoride ($B\,F_3$).

Appendix to Chapter XV.

PROBLEMS.

98. What is the weight of a cubic centimetre of bromine vapour at 150°C and 760 mm. reduced to .0°C and 760 mm.?

99. What weight of bromine is contained in a litre of hydric bromide gas?

100. What volume of hydric iodide could be prepared from 10 grammes of iodine?

101. Six grammes of manganic peroxide are boiled with an excess of strong hydric chloride. All the chlorine thus evolved is led into a solution of potassic iodide, care being taken to employ more of this iodide than the chlorine can decompose. What weight of iodine is liberated?

102. What weight of calcic sulphate could be obtained by the action of hydric sulphate on 100 grammes of calcic carbonate?

CHAPTER XVI.

107. Sulphur (S^2, S = 32) is found in yellow crystals in several volcanic districts, mixed with strontic sulphate, &c. It is also obtained by heating pyrites, a ferric persulphide which occurs in many parts of the world, and which parts with one-third of its sulphur at a high temperature. It is introduced into commerce in broken lumps, partly also in the form of sticks, partly in the form of a powder called flowers of sulphur. The sticks are remarkable for the facility with which they crack when gently heated, even by the warmth of the hand. The flowers of sulphur are made by boiling sulphur in an iron vessel, and allowing the vapour to pass into a large chamber, where it condenses in small particles, and falls to the ground. Sulphur presents several allotropic modifications, which are distinguished from one another by their density, their melting-point, their crystalline form or state of aggregation, and their solubility.

Thus, carbonic sulphide dissolves about 75 per cent. of flowers of sulphur, the remainder being of a variety which is not soluble; and the solution deposits on evaporation clear octohedral crystals, of 2.05 density and 114.5°C melting-point. When sulphur is melted by itself, and a hole made in the crust which forms on its surface, before the whole mass has solidified, the liquid portion can be poured out, leaving a number of clear needle-shaped crystals attached to the crust. This prismatic sulphur has only a density of 1.98, and, according to Brodie, it melts at 120°C. The clear prismatic

crystals gradually become opaque by keeping, at a low temperature, and they are then supposed to have undergone a change in the state of aggregation of their particles. According to Regnault the same transformation takes place rapidly, and with elevation of temperature, when clear prismatic crystals are immersed in carbonic sulphide saturated with octohedral sulphur; and on the other hand, clear octohedral crystals become opaque when heated to a temperature of about 105°C, by passing over into an aggregate of small prismatic crystals.

When sulphur is first melted it forms a pale yellow very mobile liquid, but in proportion as it is heated to a higher temperature does its colour become darker, and its consistency thicker, until at about 250°C it is an opaque mass, so nearly solid that it cannot be poured out of the vessel containing it. At still higher temperatures it again becomes perfectly liquid. If poured into cold water in this state it remains in a soft and plastic state after cooling, and can be drawn into threads. It boils at 490°C, forming a yellowish red vapour, and metallic iron or copper burns in this vapour with great intensity.

The **vapour of sulphur** has been found to possess at the temperature of 500°C a density corresponding to $S^6 = 2$ vols.; but at a temperature of 1000°C it has density proportional to its atomic weight, viz. 32, so that there are then two atoms of sulphur in two volumes, $S^2 = 2$ vols.

Sulphur is dissolved by a solution of caustic potash, forming two compounds—potassic sulphide and hyposulphite—

$$2\,S^2 + 6\,K\,H\,O = 2\,K_2\,S + K_2\,S_2\,O_3 + 3\,H_2\,O.$$

When melted with potash at a high temperature it forms a mixture of potassic sulphide and sulphate—

$$2\,S^2 + 8\,K\,H\,O = 3\,K_2\,S + K_2\,S\,O_4 + 4\,H_2\,O.$$

In each case the sulphide combines with several atoms of sulphur, forming a potassic polysulphide, such as $S^5\,K_2$.

108. Sulphuretted Hydrogen (SH_2 = 2 vols.). Sulphur combines slowly with hydrogen at high temperatures, forming sulphuretted hydrogen gas. The compound is usually made by dissolving ferrous sulphide in dilute hydric sulphate—

$$FeS + SO_4H_2 + Aq = SH_2 + SO_4Fe + Aq;$$

or else by dissolving native antimonious sulphide (in lumps) in strong hydric chloride, by the aid of heat. The evolution of the gas ceases as soon as the source of heat is withdrawn—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The gas has a most fœtid smell when present even in the proportion of one per cent. of the air, and produces poisonous effects when inhaled in quantity. Its density is 17. A pressure of about 16 atmospheres is sufficient to liquefy it at the temperature of 15°C. The gas burns with a pale blue flame, two volumes of it combining with three volumes of oxygen, forming sulphurous acid and water. Water at 0°C dissolves 4.37 times its volume of the gas, at 10°C about 3.5 volumes, and 2.9 at 20°C. The solution is gradually oxidized by contact with the air, sulphur being deposited.

Potassium heated in sulphuretted hydrogen gas decomposes it with evolution of hydrogen, forming a compound called potassic sulph-hydrate—

$$SH_2 + K = SHK + H.$$

The second atom of hydrogen can also be replaced by the further action of potassium, forming potassic sulphide—

$$SHK + K = SK_2 + H.$$

These same compounds are formed by the action of sulphuretted hydrogen on a solution of potassic hydrate. An excess of the gas forms potassic sulph-hydrate, but when this is mixed with an equivalent quantity of potassic hydrate the mixture is found to possess the properties of potassic sulphide; $SHK + OHK = SK_2 + OH_2$.

Sulphuretted hydrogen reacts in a similar manner upon a great many other metallic oxides and hydrates, replacing their oxygen atom for atom by sulphur, and the sulphides thus formed serve by their peculiar properties for the detection of many metals when present in a solution.

109. Sulphuretted hydrogen is usually passed through any solution which has to be investigated for metals, and there are eleven common metals which form insoluble sulphides under this treatment, if the solution contain free acid. These metals are arsenic, antimony, tin, gold, platinum, silver, mercury, lead, bismuth, copper, and cadmium. The first five of these sulphides dissolve in ammonic sulphide, while the remaining six are not soluble. Iron, uranium, chromium, aluminium, cobalt, manganese, nickel, and zinc are precipitated by sulphuretted hydrogen, in presence of ammonia sufficient to neutralize all the acids present; but of these eight, two, viz. chromium and aluminium, are precipitated as hydrates, not as sulphides.

The remaining common metals, viz. barium, strontium, calcium, magnesium, potassium, and sodium, form sulphides which are soluble in water; and they accordingly remain in the solution after the precipitation of the previous groups by sulphuretted hydrogen in the acid liquid, and by ammonic sulphide in the alkaline liquid.

Sulphuretted hydrogen acts upon some oxides as a reducing agent, without giving them sulphur in lieu of the oxygen which it removes. The commonest cases of this action are those of chromic acid and ferric oxide. In presence of acid hydrogen salts these oxides are reduced with deposition of sulphur, chromic oxide being formed from one and ferrous oxide from the other—

$$2\,CrO_3 + 3\,H_2S = Cr_2O_3 + 3\,H_2O + S^3.$$

$$Fe^2O_3 + H_2S = 2\,FeO + H_2O + S.$$

A double decomposition takes place between sulphurous acid and sulphuretted hydrogen, in presence of water—

$$SO_2 + 2\,H_2S = S^3 + 2\,H_2O.$$

Strong hydric sulphate is decomposed by sulphuretted hydrogen, sulphurous acid being given off.

An exceedingly delicate and beautiful test for sulphuretted hydrogen is sodic nitro-prusside with an excess of ammonia. Sulphuretted hydrogen gives a deep purple colour to the mixture.

Hydric Persulphide (H_2S^2)—an oily precipitate—is formed when sodic bisulphide is poured gradually into hydric chloride. When separated from the liquid this precipitate gradually decomposes, giving off sulphuretted hydrogen and leaving sulphur.

110. Sulphurous Acid ($SO_2 = 2$ vols.) is the sole product of the combustion of sulphur in the atmosphere. For manufacturing purposes it is obtained mixed with nitrogen by burning pyrites (FeS_2). On a small scale it is best prepared by heating mercury or copper with strong oil of vitriol; $Hg + 2\,(SO_4H_2) = SO_4Hg + SO_2 + 2\,H_2O$.

Charcoal powder is sometimes substituted for the metal, but in that case the gas which comes off is mixed with carbonic acid.

The gas is well known for its peculiar pungent odour. Its density is exactly double that of oxygen (32), for the gas occupies the same volume as the oxygen from which it is

$$S + \boxed{O = 16}\ \boxed{O = 16} = \boxed{\frac{SO_2}{2} = 32}\ \boxed{\frac{SO_2}{2} = 32}$$

made. It dissolves readily in water: its co-efficient of absorption being at 0°C 68.86; at 10°C 51.38, and at 20°C

36.22. It dissolves still more readily in alcohol. A pressure of about two atmospheres is sufficient to liquefy the gas at 15°C, forming a limpid fluid of 1.42 density.

The salts of sulphurous acid are called sulphites. They exhibit considerable analogy of constitution with the carbonates, being of two classes—simple sulphites (such as the potassic sulphite SO_3K_2, calcic sulphite $CaSO_3$), and double sulphites (such as SO_3KH). They are decomposed by hydric chloride, sulphate, or nitrate; hydric sulphite being no doubt formed in the first instance, and then decomposed into water and sulphurous acid. Sulphites are, however, not decomposed by carbonic acid in presence of water. Sulphurous acid is used for bleaching woollen or silken fabrics, and it is an efficacious agent for preventing putrefaction and fermentation. Its silver salt is decomposed by heat in presence of water, metallic silver being deposited, and hydric sulphate remaining in the solution—

$$Ag_2SO_3 + H_2O = Ag^2 + H_2SO_4.$$

When dissolved in water it gradually absorbs oxygen from the air, and is rapidly oxidized by aqueous chlorine, iodine, or nitrous acid. At high temperatures sulphurous acid combines with oxygen, forming sulphuric acid, and it is therefore evident that if sulphur were burnt at a high temperature the product would no longer be sulphurous acid, but sulphuric acid. It is deprived of its oxygen by nascent hydrogen, and at the same time supplied with two atoms of hydrogen in place of the oxygen—

$$SO_2 + 3H^2 = SH_2 + 2H_2O.$$

Sulphurous acid combines with plumbic peroxide, forming plumbic sulphate; $SO_2 + PbO^2 = SO_4Pb$.

111. Hydric Sulphate ($SO_4H_2 = 4$ vols.), commonly called sulphuric acid. This important acid salt is prepared by the action of sulphurous acid on hydric nitrite. Every

molecule of sulphurous acid requires two molecules of the nitrite from which it liberates nitric oxide—

$$S O_2 + 2 H N O_2 = H_2 S O_4 + 2 N O.$$

The nitric oxide liberated at the end of the reaction is reconverted into hydric nitrite by the action of moist air according to the equation—

$$2 N O + H_2 O + O = 2 H N O_2;$$

and by supplying air and allowing the substances time to act on one another, a small quantity of nitric oxide thus suffices to aid the formation of a large quantity of hydric sulphate. The manufacture is carried on in vast leaden chambers, constantly supplied at one end with air partially deprived of its free oxygen by burning sulphur or pyrites, and with this air the vapour of strong hydric nitrate. Steam is blown into the chamber to aid the combination, and the residual nitrogen and nitric oxide escape at the farther end by a flue. To recover the hydric nitrite this air is sometimes made to pass over a large surface of coke, wetted with strong hydric sulphate.

The dilute acid thus obtained is evaporated first in leaden pans; but the evaporation is completed in platinum or glass retorts; the water which is distilled off, together with a small quantity of acid carried over as spray, being collected for use in the chambers. The acid thus obtained, commonly called oil of vitriol, is of the composition $S O_4 H_2$, and density 1.842. It boils at 327°C. It is very liable to contain a little plumbic sulphate in solution, and ought to be distilled in a platinum retort if required in a state of purity.

By limiting the temperature during evaporation to 205°C an acid is obtained of density 1.78, and consisting of $S O_4 H_2 O H_2$, which crystallizes at temperatures below 9°C. By evaporating a dilute acid at 100° a compound is obtained $S O_4 H_2 (O H_2)_2$, of density 1.62.

112. The **vapour of sulphuric acid** (hydric sulphate) has a density of 24.5, which corresponds to $S O_4 H_2 = 4$ vols. There are strong reasons for believing that it contains two molecules ($S O_3$ and $H_2 O$) uncombined with one another, for even below its boiling-point the acid loses water, and steam has been diffused out of the vapour of the acid.

When passed through a red-hot tube the vapour of sulphuric acid is in part decomposed into sulphurous acid and oxygen gas. The sulphates are also decomposed by contact with organic matter, especially if metals capable of combining with sulphur be present.

Great heat is evolved when hydric sulphate is mixed with water, and most organic bodies containing the elements of water are decomposed by contact with the concentrated sulphate. Thus sugar is blackened and destroyed by it; even alcohol is charred and burnt by heating with sufficient oil of vitriol [n].

Sulphuric acid forms with baryta a salt perfectly insoluble in water or in hydric chloride, and the presence of a sulphate is best detected by this test. The baric sulphate is reduced by charcoal at a red heat, forming baric sulphide, which gives off sulphuretted hydrogen by the action of acids—

$$Ba S O_4 + 4 C = Ba S + 4 C O.$$

[n] Examples of sulphates and double sulphates:—

Hydric sulphate, $H_2 S O_4$.
Potassic sulphate, $K_2 S O_4$.
Sodic sulphate, $Na_2 S O_4$.
Argentic sulphate, $Ag_2 S O_4$.
Hydropotassic sulphate, $H K S O_4$.
Mercurous sulphate, $Hg_2 S O_4$.
Mercuric sulphate, $Hg S O_4$.
Cupric sulphate, $Cu S O_4$.
Stannous sulphate, $Sn S O_4$.
Ferrous sulphate, $Fe S O_4$.
Ferric sulphate, $Fe^2 (S O_4)_3$.
Aluminic sulphate, $Al^2 (S O_4)_3$.
Stannic sulphate, $Sn (S O_4)_2$.
Platinic sulphate, $Pt (S O_4)_2$.

Hydr-aluminic sulphate, $H_2 Al^2 (S O_4)_3$.
Potassio-aluminic sulphate, $K_2 Al^2 (S O_4)_3$.
Hydro-bismuthic sulphate, $H Bi (S O_4)_2$.
Potassio-ferrous sulphate, $K_2 Fe (S O_4)_2$.
Zinc-aluminic sulphate, $Zn Al^2 (S O_4)_4$.

113. Sulphuric Acid ($SO^3 = 2$ vols.) can be obtained by decomposing oil of vitriol by phosphoric acid, or by heating sodic disulphate ($Na_2S_2O_7$). SO^3 passes over while the normal sodic sulphate Na_2SO_4 remains behind. The acid can also be obtained by distilling ferric oxy-disulphate; $Fe_2O(SO_4)_2 = Fe^2O_3 + 2SO^3$. It is a white solid, similar in appearance to asbestos. Its density is 1.9. It boils a little above 50°C, and evaporates in large quantities at the common atmospheric temperature, forming dense white fumes, by combining with the moisture of the air.

When brought in contact with a small quantity of water, it combines with explosive violence, giving off a great deal of heat. It decomposes organic bodies very rapidly, liberating carbon. It also combines with nitric oxide. With dry ammonia it combines very slowly, but the addition of water causes instant combination.

Nordhausen Acid. There is a remarkable compound containing the elements of sulphuric acid added to those of hydric sulphate. It is also known by the name of **fuming sulphuric acid.** Its composition is represented by the formula $S_2O_7H_2$. It may be considered as a compound of SO_3 and SO_4H_2, for at a very gentle heat it can be separated into these two bodies, SO_3 distilling over, and SO_4H_2 remaining behind. The fuming acid is made by distilling ferric oxy-disulphate ($Fe_2O_3 . (SO_3)_2$), and collecting the acid which comes over in receivers containing some hydric sulphate.

Appendix to Chapter XVI.

PROBLEMS.

103. What weight of sulphur is contained in a litre of sulphuretted hydrogen?

104. What volume of oxygen is required for the combustion of a cubic centimetre of sulphuretted hydrogen? What is the volume of each product?

105. What weight of antimonious sulphide is required for the preparation of 500 grammes of sulphuretted hydrogen?

106. What volume of sulphurous acid is formed by the combustion of 10 grammes of sulphur?

107. What weight of sulphurous acid is required for the neutralization of 100 grammes of potassic hydrate?

108. Ascertain from the tables the percentage of sulphuric acid in a solution of 1.6 density, and calculate what weight of that solution must be used for the neutralization of 10 grammes of lime (Ca O).

109. What volume of air is needed for the complete oxidation of a kilogramme of sulphur?

CHAPTER XVII.

114. Sulphamic Acid ($SO_2(NH_2)(HO)$). The compound formed by the slow combination of ammonia with sulphuric acid, is an ammonic salt corresponding to the above-mentioned hydrogen salt. The salt does not precipitate salts of baryta, but by combining with the elements of one molecule of water it is transformed into hydr-ammonic sulphate—

$$SO_3NH_3 + H_2O = SO_4H(NH_4).$$

Sulphamide ($SO_2(NH_2)_2$) is formed by the action of ammonia on chloro-sulphuric acid—

$$SO_2Cl_2 + 2NH_3 = SO_2(NH_2)_2 + 2HCl.$$

The hydric chloride which is formed unites immediately with ammonia. This amide may be compared to urea, which is formed by a similar reaction from chloro-carbonic acid and ammonia.

Carbamic Acid ($CONH_2HO$) is a hydrogen salt which stands to carbamide in the same relation in which sulphamic acid stands to sulphamide, but it is chiefly known in combination with organic bodies.

115. Hyposulphurous Acid (S^2O_2) is only known in combination with metals in the hyposulphites. Its sodic salt is much used by photographers, as it dissolves argentic iodide. When the hydrogen salt $H_2S^2O_3$ is liberated by hydric chloride from a solution of this salt, it decomposes almost immediately, depositing sulphur and giving off sulphurous acid. The silver salt of hyposulphurous acid

decomposes rapidly, forming hydric sulphate and argentic sulphide—

$$S^2O_3Ag_2 + H_2O = SAg_2 + SO_4H_2.$$

Hyposulphuric Acid (S^2O^5) is only known in the hyposulphates. Its hydrogen salt is prepared in solution by adding dilute hydric sulphate to the solution of baric hyposulphate so as to precipitate the baryta from it without leaving any sulphate in excess. The dilute acid is evaporated in vacuo over oil of vitriol.

Its baryta salt (S^2O_6Ba) is remarkable for being soluble in water. When the salt is heated by itself it decomposes, giving off sulphurous acid and leaving baric sulphate. A similar decomposition occurs when a solution of baric hyposulphate is heated with hydric chloride; baric sulphate is deposited while sulphurous acid is liberated.

The other three acids of sulphur—viz. monosulphuretted hyposulphuric acid (S^3O^5), disulphuretted hyposulphuric acid (S^4O^5), and trisulphuretted hyposulphuric acid (S^5O^5)—form compounds which have been but little studied.

116. Ammonic Sulphide ($S(NH_4)_2$) can be obtained by mixing one volume of sulphuretted hydrogen with two volumes of ammonia, and passing the mixture into a tube cooled to $-18°$; or more easily by heating a mixture of sal-ammoniac and potassic sulphide and condensing at $-18°C$. It is a colourless salt which decomposes at $0°C$, giving off ammonia and leaving $SH(NH_4)$ hydr-ammonic sulphide.

A solution of the compound is usually prepared by dividing a given quantity of ammonia into two equal portions, saturating one portion by sulphuretted hydrogen, thereby forming $SH(NH^4)$, and then mixing it with the other portion. The solution is exceedingly alkaline, and rapidly turns yellow in contact with the air, by absorbing oxygen, and forming a mixture of ammonia and ammonic persulphide, which decomposes further, forming tersulphide and hyposulphite.

Hydric sulphate forms two salts with ammonia—the normal sulphate $SO_4(NH_4)_2$, which crystallizes in the same form as the normal potassic sulphate SO_4K_2. The other compound is the double sulphate $SO_4H(NH_4)$. Sulphurous acid forms two similar ammonia salts – $SO_3(NH_4)_2$ and $SO_3H(NH_4)$.

117. Carbonic Sulphide ($CS_2 = 2$ vols.). This compound is the analogue of carbonic acid, and it is sometimes called sulpho-carbonic acid. It is made by burning red-hot carbon in sulphur vapour. It is an oil, insoluble in water, and of a density of 1.26. It boils at 45°C, and its vapour has the same volume as carbonic acid, and accordingly a density of 38. Its odour is exceedingly offensive, and is said to produce very injurious effects upon persons frequently exposed to it. It burns with a pale blue flame. Carbonic sulphide combines with the sulphides of many basic metals, such as potassic sulphide, forming compounds analogous to those which carbonic acid forms on combining with basic oxides. These compounds are called sulpho-carbonates. They are decomposed in presence of water by strong acids, a compound of carbonic sulphide with sulphuretted hydrogen being formed. This compound—

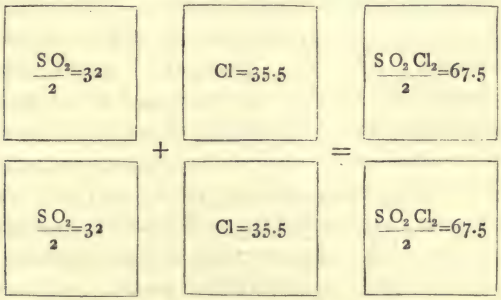
118. CS_3H_2 is the true **hydric sulpho-carbonate.** Ammonia solution decomposes carbonic sulphide, forming sulphuretted hydrogen and an acid compound analogous to hydric cyanate, and differing from it only by having an atom of sulphur in place of the atom of oxygen in the cyanate. This body is a valuable re-agent. It is called **hydric sulpho-cyanate,** $CS_2 + NH_3 = CNSH + SH_2$.

These products combine with ammonia, forming ammonic sulpho-cyanate and ammonic sulphide. Ammonic sulpho-cyanate forms a deep blood-red compound when mixed with a solution of ferric salt. The red compound consists of ferric sulpho-cyanate ($Fe^2(CNS)_6$).

There are two chlorides of sulphur—**hyposulphurous subchloride** ($S^2 Cl_2 = 2$ vols.), obtained by passing dry chlorine into flowers of sulphur, and distilling off from the sulphur which is dissolved. It is a yellow liquid of unpleasant odour, and emits fumes in moist air. Its density is 1.68, and it boils without decomposition at 138°C. In contact with water it is decomposed, forming hydric chloride, while the sulphur is partly deposited in the free state, partly combined with oxygen as sulphurous acid.

Hyposulphurous Chloride ($S Cl_2$) is obtained by saturating the subchloride with chlorine, and distilling in a stream of chlorine. The compound gives off chlorine when heated, and is partially reduced to subchloride. It is decomposed by water like the subchloride.

119. Chlorosulphuric Acid ($S O_2 Cl_2 = 2$ vols.) is formed by the combination of equal volumes of chlorine and sulphurous acid.



A more convenient way of making it is by decomposing hydric sulphate by an excess of phosphoric chloride—

$$S O_4 H_2 + 2 P Cl_5 = S O_2 Cl_2 + 2 P O Cl_3 + 2 H Cl.$$

The liquid boils at 80°, and has a density of 1.68. It is decomposed gradually by water, forming one molecule of the sulphate and two molecules of hydric chloride—

$$S O_2 Cl_2 + 2 H_2 O = S O_4 H_2 + 2 H Cl.$$

It is to be considered as hydric sulphate in which $(H O)_2$ is replaced by Cl^2.

Chlorohydrated sulphuric acid ($S O_2 Cl H O$) is the first product of the action of phosphoric chloride on hydric sulphate; $S O_4 H_2 + P Cl_5 = S O_3 H Cl + P O Cl_3 + H Cl$; and in its composition it is intermediate between hydrated sulphuric acid and chlorosulphuric acid. It is also formed by the action of hydric chloride gas on sulphuric acid. The acid does not combine with more than one molecule of hydric chloride, and only sluggishly with so much—

$$S O^3 + H Cl = S O_2 Cl (H O).$$

It appears to form salts, but owing to their instability they have been but little studied. The sodium salt is obtained by the combination of sodic chloride with sulphuric acid.

120. Selenium (Se = 79·5). This rare element is chiefly of interest from its analogy with sulphur. The element can be reduced from its oxide ($Se O_2$), called selenious acid, by the action of sulphurous acid in solution. It goes down in the form of a red powder, which can be melted at a temperature somewhat over 100°C. It is a dark brown substance of 4·3 density, very friable. It evaporates at a higher temperature than sulphur, and produces, even when present in air in small quantities, an odour like horse-radish. Selenium combines in two proportions with oxygen, forming selenious acid and selenic acid, corresponding to sulphurous and sulphuric acids. It is not improbable that the volatile substance which is formed at the same time with selenious acid by the combustion of selenium in the air may be a lower oxide of selenium.

Selenious acid is precipitated from its solutions by sulphuretted hydrogen—

$$Se O_2 + 2 H_2 S = Se S_2 + 2 H_2 O;$$

and the selenious sulphide so obtained is a sulphur acid, and forms numerous sulphur salts called sulpho-selenites. Selenic acid has great resemblance to sulphuric acid, and forms

many salts, such as $Na_2 Se O_4$, which are undistinguishable, in their crystalline form, from the corresponding sulphates. Baric seleniate is insoluble in water, but dissolves with evolution of chlorine in boiling hydric chloride, and can thereby be distinguished from baric sulphate—

$$Ba Se O_4 + 4 H Cl = Se O_2 + Ba Cl_2 + 2 H_2 O + Cl^2.$$

Seleniuretted Hydrogen ($Se H_2 = 2$ vols.) is prepared in a similar manner to sulphuretted hydrogen, and shews considerable resemblance to that body in its action on solutions of metallic salts.

121. Tellurium (Te = 129) is a rare divalent element, of metallic appearance, and of a density of about 6.2. It melts at a higher temperature than lead, and can be volatilized at a red heat. Tellurium conducts electricity, whereas sulphur and the ordinary kind of selenium are non-conductors. It can be precipitated by zinc from solutions, like a weak metal. In spite of these facts chemists are agreed to place tellurium in the same family with oxygen, sulphur, and selenium, on account of the close analogy which its compounds exhibit with those of selenium.

Tellurous acid dissolves in hydric chloride, but very slightly in water; it is precipitated from acid solutions by sulphuretted hydrogen—

$$Te O_2 + 2 H_2 S = Te S_2 + 2 H_2 O;$$

and tellurium is reduced from it by a solution of sulphurous acid. **Telluric acid** forms with baryta a salt which, although insoluble in water, is soluble in hydric nitrate, and tellurium is thus separated from selenium.

Hydric tellurate crystallizes readily in combination with two molecules of water—

$$Te O_4 H_2 (O H_2)_2.$$

The acid ($Te O_3$) is obtained by heating the hydrogen salt. It is insoluble in water, and dissolves with great difficulty in potash.

CHAPTER XVIII.

122. Phosphorus ($P = 31$, $P^4 = 2$ vols.). Phosphorus is usually made from bone-earth (the ashes of bones). This material consists mainly of calcic phosphate ($P_2 O_8 Ca_3$), and when it is acted upon by dilute hydric sulphate a part of the lime is removed as calcic sulphate, which can be filtered off from the soluble double-phosphate, commonly called superphosphate of lime—

$$P_2 O_8 Ca_3 + 2 H_2 S O_4 = P_2 O_8 Ca H_4 + 2 Ca S O_4.$$

The solution is evaporated to dryness with charcoal and the mixture heated in stoneware retorts. Carbonic oxide is formed, and phosphorus distils over, and is collected under water to protect it from the air. Calcic phosphate remains in the retort.

$$3 H_4 Ca P_2 O_8 + 10 C = P^4 + 10 C O + Ca_3 P_2 O_8 + 6 H_2 O.$$

Phosphorus is generally cast into sticks, and sent out for sale under water in tin cases. It is a clear colourless substance of 1.83 density. It melts at 45°C, and is easily cast into moulds under water, as it does not dissolve in that liquid. A stick of phosphorus when exposed to the air emits a faint light, visible in a dark room; and when it is gently rubbed against a hard surface luminous marks are left. The experiment is however exceedingly dangerous, as phosphorus catches fire when rubbed, and produces painful burns which heal with difficulty. It should always be cut under water.

In summer weather it has the consistency of wax; in winter it is brittle. It boils at 290°C, and its vapour has

a density of 62, proving that two atoms of phosphorus occupy the same volume as one atom of hydrogen. Phosphorus dissolves readily in carbonic sulphide, and can be obtained in crystals from that solution. It is dissolved by hot aqueous solutions of potash, soda, lime, &c., and on dissolving in them it gives off a gas which catches fire by mere contact with air, and burns with a white flame, forming phosphoric acid and water. Another part of the phosphorus is found in the solution, in the form of potassic hypophosphite—

$$P^4 + 3\,K\,H_3\,O_2 = P\,H_3 + 3\,K\,P\,O_2\,H_2;$$

other products are formed at the same time.

123. When phosphorus is heated to a temperature of 240° it gradually forms a red deposit, and if the heat be continued long enough nearly all the phosphorus is transformed into this red substance. At a still higher temperature the red powder evaporates, and its vapour on condensation yields common clear phosphorus, similar to that obtained by distilling the clear phosphorus itself. The red powder is nothing else than phosphorus in an allotropic state. It is most conveniently separated from common phosphorus by carbonic sulphide, in which **red phosphorus** is quite insoluble. Caustic soda is used by the manufacturers of red phosphorus to purify it from clear phosphorus. The most convenient way to prepare red phosphorus in small quantities is that discovered by Brodie, viz. to dissolve some phosphorus in carbonic sulphide, with a small quantity of iodine, and heat the solution to 100°C in a sealed-up tube for some time. The red phosphorus is then deposited from the liquid in proportion as it is formed.

Red phosphorus is less active chemically than clear phosphorus, and all differences between the two varieties are connected with this one. Red phosphorus requires a much higher temperature for its ignition in the air than that at

which clear phosphorus kindles into flame. The heat of combustion of clear phosphorus is to that of red phosphorus in the proportion of 1.15 to 1. The specific heat of red phosphorus is also less than that of the clear variety, the former being 0.1700, the latter 0.1887. The density of red phosphorus is usually about 2.1.

A stick of clear phosphorus decomposes cupric sulphate when immersed in a solution of the salt, becoming coated with metallic copper, while the phosphorus dissolves as hydric phosphate. Red phosphorus made by heat has no such action.

The red phosphorus made by the action of iodine exhibits an interesting anomaly when distilled, for its vapour condenses in great part in the form of red phosphorus. This result is due to the presence of a trace of iodine, which remains in the phosphorus and evaporates with it. This iodine causes the change of clear phosphorus into red, in proportion as it condenses from the vapour. Red phosphorus does not emit light when exposed to the air, and does not undergo the slow combustion which occurs with clear phosphorus, and to which the phosphorescence is owing.

Both kinds of phosphorus burn in oxygen, sulphur, or chlorine, and form two compounds with each of these elements, viz. P_2O_3, P_2O_5; P_2S_3, P_2S_5; PCl_3, PCl_5. Some compounds with less sulphur are also known. The element can also be obtained in combination with hydrogen and the metals; for instance, phosphuretted hydrogen is PH_3, and there are two cupric phosphides, P_2Cu_3 and P_2Cu_6.

124. Phosphoric Acid (P_2O_5) is made by burning phosphorus in dry air, taking care to supply the air in abundance. It is a snow-like powder, and is volatile at a high temperature. It combines with water very energetically, and takes it from most compounds in which the elements of water are contained. Each molecule of the acid combines with three

molecules of water, forming two molecules of the hydrated acid PO_4H_3—

$$P_2O_5 + 3H_2O = 2H_3PO_4;$$

and this water can be but partially expelled by heat. By exposing the hydrate to a red heat in a platinum dish, a vitreous-looking mass is obtained, which is generally called glacial phosphoric acid, and which retains one-third of the hydrogen of the original salt—

$$PO_4H_3 = PO_3H + H_2O.$$

A recently prepared solution of glacial phosphoric acid in cold water carefully neutralized by ammonia gives a white precipitate with argentic nitrate: thus,

$$PO_3NH_4 + NO_3Ag = PO_3Ag + NO_3NH_4;$$

but if the solution be boiled for some time with plenty of water, and then neutralized and precipitated by argentic nitrate, it gives a bright yellow precipitate containing three times as much silver as the white precipitate—

$$PO_4(NH_4)_3 + 3AgNO_3 = PO_4Ag_3 + 3NH_4NO_3.$$

125. Hydric Phosphate, commonly called phosphoric acid (PO_4H_3), is most conveniently prepared by dissolving phosphorus in dilute hydric nitrate, with the aid of heat. The operation is usually performed in a glass retort, provided with a condenser, as a good deal of hydric nitrate evaporates with the nitrite during the operation. The phosphorus dissolves gradually, but to ensure its being fully oxidized some hydric nitrate should be added after the phosphorus has disappeared, and the whole then evaporated to a syrupy consistence.

The phosphate can also be prepared from bone-earth. For that purpose the bone-earth is decomposed by hydric sulphate, as for the preparation of phosphorus, and the filtered solution of hydro-calcic phosphate is neutralized by ammonia. The effect of this is to form triammonic

phosphate, which remains in the solution, and to precipitate calcic phosphate—

$$3\,H_4\,Ca\,P_2\,O_8 + 12\,N\,H_3 = Ca_3\,P_2\,O_8 + 4\,(N\,H_4)_3\,P\,O_4.$$

The solution is filtered off from the precipitate of calcic phosphate, evaporated to dryness and heated to redness in a platinum vessel. The ammonia is entirely expelled by the heat, and the residue is glacial phosphoric acid[o], ready for solution.

Hydric phosphate is tribasic. With potassium it forms two double salts, hydro-dipotassic phosphate $H\,K_2\,P\,O_4$, and di-hydro-potassic phosphate H_2KPO_4, besides the normal salt $K_3\,P\,O_4$. There are similar salts with sodium. The force with which the first atom of hydrogen is replaced is greater than that with which the second is replaced, and the third atom of potassium is taken up so feebly that the presence even of carbonic acid is sufficient to prevent potash from reacting on the hydro-dipotassic phosphate[p].

[o] This glacial acid has a composition represented by the formula $H\,P\,O_3$.

[p] Examples of phosphates:—

Calcic phosphate, $Ca_3\,(P\,O_4)_2$.
Di-hydro-calcic phosphate, $H_2\,Ca_2\,(P\,O_4)_2$.
Tetra-hydro phosphate, $H_4\,Ca\,(P\,O_4)_2$.
Ammonio-magnesic phosphate, $N\,H_4\,Mg\,P\,O_4$.
Microcosmic salt, $H\,N\,H_4\,Na\,P\,O_4$.
Ferrous phosphate, $Fe_3\,(P\,O_4)_2$.
Ferric phosphate, $Fe_2\,P_2\,O_8$.
Apatite (calcic fluoro-tri-phosphate), $Ca_5\,Fl\,(P\,O_4)_3$.

CHAPTER XIX.

126. Di-hydro-sodic phosphate ($H_2 Na P O_4$) is decidedly acid to test-paper, and it expels carbonic acid from sodic carbonate with brisk effervescence, forming the hydro-di-sodic, or common phosphate, $H Na_2 P O_4$. But this common phosphate, containing two atoms of sodium and one of unreplaced hydrogen, is no longer acid to test-paper, indeed it is faintly alkaline. The normal phosphate, containing three atoms of sodium, is perfectly alkaline to test-paper, and when dissolved in water it absorbs carbonic acid from the air, like caustic soda.

Although the molecule of hydric phosphate combines with three molecules of soda it must be admitted only to neutralize two molecules, as the alkaline properties of the third molecule of soda are maintained in the normal salt.

The basic hydrogen of hydric phosphate is sometimes replaced partly by one basic metal, partly by another; thus, a common salt, called **microcosmic salt**, contains sodium, ammonium, and hydrogen, combined as basylous metals in one molecule of the phosphate. Its formula is—

$$P O_4 Na N H_4 H.$$

When the phosphate is neutralized by ammonia it can be fully precipitated from its solution by the addition of magnesic sulphate. The precipitate consists of a molecule of the hydrogen salt, in which two atoms of hydrogen are replaced by one atom of magnesium, while the third atom of hydrogen is replaced by ammonium ($P O_4 Mg N H_4$). In the

determination of phosphoric acid this salt is precipitated, but before weighing, it is ignited, whereby ammonia and water are driven off, and magnesic pyrophosphate remains—

$$2\,Mg\,N\,H_4\,P\,O_4 = Mg_2\,P_2\,O_7 + 2\,N\,H_3 + H_2\,O.$$

Phosphoric acid forms with ferric oxide a salt which is valuable for being insoluble in hydric acetate. The salt is easily obtained by precipitating a soluble phosphate by ferric chloride. Its composition is represented by the formula $P_2\,O_8\,Fe_2$. In presence of acid hydrogen salts, a phosphate can be detected by the yellow precipitate which it forms with ammonic nitro-molybdate.

A common acid phosphate does not coagulate albumen. And in this respect it resembles a pyrophosphate ($H_4\,P_2\,O_7$), and differs from a metaphosphate ($H\,P\,O_3$)^n.

127. Tetrahydric Diphosphate, commonly called pyrophosphoric acid ($P_2\,O_7\,H_4$). By heating common hydro-disodic phosphate to a bright red heat the salt is deprived of its basic water, and transformed into the pyrophosphate $P_2\,O_7\,Na_4$. Phosphates of this constitution can be distinguished from common phosphates partly by the lesser solubility of the sodium salt ($Na_4\,P_2\,O_7$), partly also by the white colour of the silver salt ($P_2\,O_7\,Ag_4$). The tetra-hydric diphosphate resembles common phosphate, however, in the circumstance that when added to baric chloride, or to argentic nitrate, it produces no precipitate; the neutralization by an alkali is necessary for the formation of either precipitate.

Metaphosphate ($P\,O_3\,H$)^n. The glacial acid has this composition, but there appear to be several varieties of it, differing from one another in molecular weight, some being higher multiples of the formula $P\,O_3\,H$ than others.

Pyrophosphates, as well as these metaphosphates, are converted into the common tribasic salt by long boiling

with water, in an acid liquid; or by fusion with an excess of caustic alkali.

128. Phosphorous Acid (P_2O_3) can be obtained by burning a piece of phosphorus in a glass tube, with very limited supply of dry air. It is more volatile than phosphoric acid. It dissolves readily in water, forming hydric phosphite (PO_3H_3); but when the solution is evaporated to dryness, and heated, for the purpose of driving off the water, the acid is decomposed, evolving phosphuretted hydrogen, and forming hydric phosphate.

A solution of the phosphite is most conveniently prepared by decomposing phosphorous chloride by water—

$$P Cl_3 + 3 H_2O = P O_3 H_3 + 3 H Cl.$$

The hydric chloride is expelled by evaporation. Hydric phosphite is dibasic; for no more than two of its atoms of hydrogen can be replaced by potassium, or sodium, or other basic metals; and in the double phosphites only one-third of the hydrogen of the acid salt is replaced by one metal.

It reduces silver, gold or mercury from solutions of their salts. With mercuric chloride the first action consists in precipitating calomel—

$$P O_3 H_3 + 2 Hg Cl_2 + H_2O = P O_4 H_3 + Hg^2 Cl_2 + 2 H Cl.$$

Hypophosphites ($P O_2 H_3$). It was mentioned above that a salt of this acid is formed by boiling phosphorus in potash or baryta, &c. When baryta is used, all the phosphate and phosphite formed go down as baryta salts; baric hypophosphite alone remaining in solution with the excess of base. The acid is monobasic, two of its three atoms of hydrogen being unreplaceable by basic metals. The barium salt is accordingly represented by the formula $(P O_2 H_2)_2 Ba$; and the potassic hypophosphite is $P O_2 H_2 K$.

In contact with nascent hydrogen hypophosphites in an acid solution evolve phosphuretted hydrogen. A phosphite gives rise to the same product when similarly treated. Cupric

hypophosphite undergoes a remarkable decomposition when a solution of the salt is allowed to stand for a few hours. A red-brown powder, consisting of cuprous hydride, is deposited from the salt, together with metallic copper. The cuprous hydride dissolves easily in hydric chloride, with evolution of hydrogen, a property which metallic copper does not possess—

$$Cu^2 H_2 + 2\,H\,Cl = Cu^2 Cl_2 + 2\,H^2.$$

129. Phosphuretted Hydrogen ($P H_3 = 2$ vols.) is a gas analogous to ammonia, but possessing feebler basic properties. It is easily obtained by heating hydric phosphite. The gas has an unpleasant smell of rotten fish. It is easily condensed by pressure to a liquid. With an equal volume of hydric iodide gas it combines, forming a salt, which crystallizes in beautiful cubical crystals, and is represented by the formula $P H_4 I$. This salt is decomposed by water into hydric iodide, which dissolves, and phosphuretted hydrogen, which is liberated. Pure phosphuretted hydrogen is not spontaneously inflammable, but it can easily be kindled, and burns with a bright flame.

When phosphuretted hydrogen is formed by the action of phosphorus on aqueous potash, it contains another compound which is spontaneously inflammable. This compound can be condensed to the liquid state by cold, and is said to have the composition $P_2 H_4$; but it requires further investigation.

130. Phosphorous Chloride ($P Cl_3 = 2$ vols.). Clear phosphorus burns vividly, but with a pale flame, in dry chlorine; and if the product be distilled with an excess of phosphorus it constitutes a liquid of 1.45 density, and boiling without decomposition at 78°C. Phosphorous chloride fumes in the air, and decomposes water rapidly. It decomposes many oxides and hydrated oxides, in a manner similar to that in which it decomposes water, chlorine combining with

hydrogen, or with any substance like hydrogen, and the phosphorus forming a phosphite such as hydric phosphite ($P O_3 H_3$).

Phosphoric Chloride ($P Cl_5 = 4$ vols.) is easily obtained from phosphorus, or from the phosphorous chloride, by the action of chlorine. It is a solid crystalline compound, and breaks up on distillation into phosphorous chloride and free chlorine, which reunite rapidly at the lower temperature of the condenser. This compound is one of the most powerful agents for the decomposition of oxides.

With a small quantity of water it decomposes into a liquid compound called chlorophosphoric acid, while hydric chloride is given off. The reaction is as follows:—

$$P Cl_5 + H_2 O = P O Cl_3 + 2 H Cl;$$

and chlorophosphoric acid is in its turn readily decomposed by water, forming hydric-phosphate and chloride—

$$P O Cl_3 + 3 H_2 O = P O_4 H_3 + 3 H Cl.$$

It is probable that the first reaction is

$$P O Cl_3 + H_2 O = P O_2 Cl + 2 H Cl,$$

and that this chloride reacts on another molecule of water,

$$P O_2 Cl + H_2 O = P O_3 H + (H Cl),$$

leaving the metaphosphate to take up a molecule of water, and to become tribasic salt.

Ammonia decomposes phosphoric chloride, forming amongst other products the phosphoric chloronitride $P_3 N_3 Cl_6$.

Chlorophosphoric Acid has a vapour density of 78.75; for its molecule $P O Cl_3$ occupies two volumes. In the liquid state it has a density of 1.7, and it boils at 110°C.

Sulphuretted hydrogen decomposes phosphoric chloride in the same way that water does—

$$P Cl_5 + H_2 S = P S Cl_3 + 2 H Cl.$$

Bromine combines with phosphorus in a similar manner

to chlorine, forming phosphorous bromide ($P Br_3$) or phosphoric bromide ($P Br_5$).

Iodine has not been found to form phosphoric iodide. It forms however phosphorous iodide, which crystallizes from sulphide of carbon, and also a beautiful crystalline biniodide ($P^2 I^4$). Both of these iodides of phosphorus act upon oxides in the same sort of way as the chlorides of phosphorus do. But owing to the slight force with which iodine combines with hydrogen or bodies like hydrogen, the reactions are less violent.

131. There are three well-characterized **sulphides of phosphorus,** $P_2 S$, $P_2 S_3$, and $P_2 S_5$; all of which combine with alkaline sulphides, forming sulphur salts, corresponding to the oxygen salts of hypophosphorous, phosphorous, and phosphoric acids.

Clear phosphorus and sulphur combine with such violence that considerable care should be taken in bringing the two elements together. With red phosphorus the action is however much more tranquil and convenient, and the sulphides are best made from this kind of phosphorus. Both phosphorous sulphide and phosphoric sulphide are decomposed by water, with formation of hydric phosphite and phosphate respectively. Berzelius investigated and described a hypophosphorous subsulphide ($P_4 S$).

CHAPTER XX.

132. Boron (B = 11) is reduced from boracic acid, or from boric fluoride, by sodium. Freshly prepared boron dissolves in water, but after exposure to a white heat it is insoluble. The black powder thus obtained is as infusible as lamp-black, and cannot be volatilized.

Deville and Wöhler have obtained boron in the form of crystals by allowing it to be deposited from solution in melted aluminium.

Only one compound of boron with oxygen is known, viz. boracic acid (B_2O_3).

This acid can be prepared from commercial borax, which is a sodic diborate. The salt is dissolved in water with the aid of heat, and gradually decomposed by hydric sulphate. The necessary quantity of the acid salt can be estimated by the action of the liquid on blue litmus-paper. Hydric borate imparts to the paper a dull red colour, but as soon as all the borax is decomposed and a little additional acid sulphate added to the liquid, a bright red colour immediately makes its appearance, and indicates the completion of the decomposition. On the liquid becoming cool, hydric borate (BO_3H_3) crystallizes out from it, and can be purified by recrystallization. The borate easily gives up its water when melted in a platinum crucible, and forms a clear glass.

Boracic acid evaporates readily in a current of steam, and is collected by condensation of steam in some volcanic districts of Tuscany. It imparts to flame a green colour. No

borate can be completely precipitated from a solution by any known process; and detection and estimation of a borate in mixtures are operations of some difficulty.

The majority of the borates can be represented on the same plan as hydric borate, $B_2H_6O_6$, and the following series is known, in which sodium replaces successively each atom of hydrogen—

$$B^2H_6O_6,$$
$$B^2H_5NaO_6,$$
$$B^2H_4Na_2O_6,$$
$$B^2H_3Na_3O_6,$$
$$B^2H_2Na_4O_6,$$
$$B^2Na_6O_6.$$

Boric nitride (BN) is formed by direct combination of boron with nitrogen at a red heat. It is a very inert substance. It is decomposed by steam at a high temperature, forming hydric borate and ammonia.

133. Boric Chloride ($BCl_3 = 2$ vols.) is formed by passing chlorine gas through a red-hot porcelain tube containing a mixture of boracic acid and charcoal. It is a mobile liquid, boiling at 18°. In contact with water it is rapidly decomposed, forming hydric chloride and a borate—

$$BCl_3 + 3H_2O = BO_3H_3 + 3HCl.$$

Boric fluoride ($BF_3 = 2$ vols.) is obtained by the action of boracic acid upon calcic fluoride at a high temperature—

$$3CaF_2 + 4B_2O_3 = 2BF_3 + 3Ca(BO_2)_2.$$

It is a colourless gas, rapidly dissolved by water forming a dense oily liquid, called hydric fluo-borate—

$$8BF_3 + 3H_2O = B_2O_3 + 6(BF_3, HF).$$

Boric fluoride colours the flame green, and this property is used to detect minute traces of boracic acid in minerals. The finely powdered body under examination is fused on platinum wire with a mixture of fluorspar and potassic disulphate. Boracic acid is thus liberated at a high tempera-

ture, and it immediately reacts upon the fluorspar with the formation of boric fluoride.

Boric sulphide (B_2S_3) can be obtained by burning boron in sulphur. It is decomposed by water.

134. Silicon (Si = 28) is found as silicic acid (usually called silica) in the greater number of rocks. In its physical characters silicon has some resemblance to carbon and boron. It is prepared from potassic fluosilicate by the action of sodium, and if metallic zinc be present, the silicon is obtained in the form of crystals, which are not attacked by acid sulphates nor by aqueous hydric chloride. Some alloys of silicon present valuable properties, for which it seems not unlikely that they may become articles of manufacture.

Amorphous silicon decomposes gaseous hydric chloride, forming a liquid compound containing silicon, chlorine, and hydrogen. This chlorohydride of silicon boils at about 42°C, and its vapour burns as easily as ether. It has the composition $SiCl_3H$.

Silica or silicic acid (SiO_2) occurs pure as rock crystal. From felspar or any other silicate, however insoluble, the acid can be obtained by the following process. The finely powdered mineral is fused with sodio-potassic carbonate, the product dissolved in dilute hydric chloride, and the whole evaporated to dryness with an excess of that liquid. All the bases contained in the original mineral can be dissolved by hydric chloride from this dried mass, leaving the silica in the form of a fine white powder. When silica is first expelled from a solution of one of its salts, such as sodic silicate, in presence of much water, by hydric chloride, it is in the form of a hydrate soluble in water, and by placing such a mixture of silica solution and sodic chloride upon his so-called dialyzer, Professor Graham has succeeded in diffusing out all the sodic chloride and obtaining a solution of pure silicic acid in water. Such a solution gelatinizes on standing.

The aqueous solution of silicic acid probably contains the tetrahydrate $Si O_4 H_4$, but the dihydrate $Si O_3 H_2$ is also said to exist, besides others containing still less water.

At ordinary temperatures silica is a very weak acid, but at a red heat it is capable of expelling even sulphuric acid from its salts; and this must be attributed in some measure to the fact that at these high temperatures sulphuric acid evaporates readily, whereas silica cannot be volatilized, even at the highest artificial temperatures.

The composition of the **Silicates** present many varieties. Some correspond to the hydric silicate $Si O_4 H_4$—for instance, $Si O_4 Mg_2$, in which Mg_2 (two atoms of magnesium) occupy the place of the four atoms of hydrogen of the hydrate—others, such as $Si O_3 Na_2$, correspond to the lower hydrate, and there are also the following amongst other silicates—

$$Si_2 O_5 K_2, \quad Si_3 O_7 Na_2, \quad Si_4 O_9 Na_2.$$

Silicous oxide (Si O ?) is formed by dissolving silicic chlorohydride in water at 0°. It decomposes water rapidly with evolution of hydrogen in presence of alkalies, forming a silicate.

Siliciuretted hydrogen is obtained together with hydrogen by dissolving an alloy of silicon and magnesium in hydric chloride. It has also been obtained with similar properties by using a piece of aluminium alloyed with silicon as the positive pole in conducting the current of a battery through a solution of sodic chloride. Hydrogen is evolved at both poles while the positive pole combines with chlorine, and a part of its materials no doubt decomposes water. The compound is spontaneously inflammable in air.

135. Silicic Chloride ($Si Cl_4 = 2$ vols.) is formed by a similar process to that adopted in the preparation of boric chloride. It boils at 50°C, and its vapour is rapidly decomposed by moisture.

Silicic Fluoride ($Si F_4 = 2$ vols.) is readily formed by the

action of hydric fluoride on silica or any compound of silica. It is most easily prepared by heating a mixture of finely powdered glass and fluorspar in a platinum retort with fuming oil of vitriol—

$$Si O_2 + 2 Ca F_2 + 2 H_2 S_2 O_7 = Si F_4 + 2 Ca S O_4 + 2 H_2 S O_4;$$

and collecting the gas over mercury. The fluoride is readily absorbed and decomposed by water, one-third of the silicon being deposited in the form of silica, while the other two-thirds remain in combination with fluorine and hydrogen—

$$3 Si F_4 + 2 H_2 O = 2 H_2 Si F_6 + Si O_2.$$

Appendices to Chapters XVII—XX.

PROBLEMS.

110. What would be the vapour volume of 10 grammes of hydric sulphate ($H_2 S O_4$) at 400°C?

111. What volume of the vapour of carbonic sulphide, measured at 100°C and 760 mm., could you obtain by combining 100 grammes of carbon with sulphur?

112. What volume of oxygen is needed for the combustion of 10 grammes of carbonic sulphide? What volume of each product is formed?

113. What volume of nitric oxide is needed for the complete combustion of 10 grammes of carbonic sulphide?

114. What is the weight of a litre of hyposulphurous subchloride ($S_2 Cl_2$) at 200°C?

115. What volume of hydric chloride would be formed if a litre of chlorosulphuric acid vapour were decomposed by water?

116. What volume of hydric iodide would combine with a litre of phosphuretted hydrogen?

117. What volume of oxygen would be required for the

complete combustion of a cubic centimetre of phosphuretted hydrogen?

118. What volume of phosphorous chloride could be obtained by combining one litre of chlorine with phosphorus?

119. 10 grammes of phosphorus are saturated with chlorine. What is the vapour volume of the product, calculated at 0°C and 760 mm.?

120. What volume of chlorine could be taken up by a litre of phosphuretted hydrogen?

121. What volume of hydric chloride would be obtained by replacing, by an equivalent weight of hydrogen, the boron in one litre of boric chloride (calculated at 0°C)?

122. What weight of boron is contained in a litre of boric fluoride?

123. 10 grammes of silica are converted into silicic fluoride. What is the volume of the gas?

124. 50 grammes of silicic chloride are decomposed by water. What weight of dry silica is formed?

CHAPTER XXI.

136. Arsenic ($As = 75$; $As^4 = 2$ vols.) is a white and brittle metal, which evaporates easily when heated, but does not melt. Its vapour has a peculiar odour, which is compared to the odour of garlic. Arsenic burns with a blueish flame, forming arsenious acid (As_2O_3), and in moist air it undergoes gradual oxidation at the ordinary temperature. The preparation of metallic arsenic is an important test for the presence of any of its compounds, and ought to form part of the investigation in every case of poisoning by arsenic.

Arsenious acid mixed with charcoal is easily reduced by the action of heat, and the metal collects on the nearest cold place in the tube in which the mixture is heated. Another very common way of obtaining metallic arsenic is by Marsh's test. The first operation is to pour the solution of an arsenite into a mixture of metallic zinc and dilute hydric sulphate, the hydrogen which is being evolved desoxidizes the arsenite and at the same time replaces the oxygen by hydrogen. The excess of hydrogen passes off with the arseniuretted hydrogen thus formed. This compound is then decomposed by passing it through a glass tube heated strongly by a gas flame. A ring of metallic arsenic is thus obtained beyond the hot part of the tube. If the hydrogen containing the arseniuretted hydrogen be allowed to come out at a fine point in a glass tube and there kindled, it burns with a blueish flame, and a piece of cold porcelain held in the flame becomes marked by a brown spot of metallic arsenic. Arsenic

is readily dissolved by hydric nitrate, or by an aqueous solution of so-called bleaching-powder. Hydric chloride has scarcely any action upon it. There are two compounds of arsenic with oxygen—viz. arsenious acid (As_2O_3) and arsenic acid (As_2O_5).

137. Arsenious Acid is commonly sold by the name of "arsenic" or white arsenic. It usually occurs as a white crystalline powder, but it can also be obtained by fusion in the form of a glassy mass, which gradually becomes white and opaque, like porcelain. The acid dissolves slowly in water, and its solution has a feebly acid reaction; and anhydrous crystals are deposited, on cooling, from a solution saturated at the boiling-point. It dissolves readily in caustic potash, and can slowly expel carbonic acid from potassic carbonate. Aqueous hydric chloride dissolves arsenious acid readily, but on boiling this solution arsenious chloride is volatilized. Aqueous arsenious acid is precipitated by an excess of lime-water, the precipitate having a composition represented by the formula AsO_3CaH. A solution of argentic nitrate is scarcely affected by an aqueous solution of arsenious acid, but the careful addition of ammonia causes the precipitation of yellow argentic arsenite—

$$AsO_3Ag_3.$$

Sulphuretted hydrogen causes a yellow colour in an aqueous solution of arsenious acid, and yellow arsenious sulphide is precipitated from the mixture on the addition of hydric chloride; $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$.

Metallic copper immersed in a solution of arsenious acid acidulated by hydric chloride reduces the metal and becomes coated with a grey film.

Arsenious acid forms with ferric oxide a compound insoluble in water, and ferric hydrate is accordingly administered as an antidote for arsenious acid.

138. Arsenic Acid (As_2O_5) is readily obtained by the

action of hydric nitrate on arsenious acid. It is a much stronger acid than arsenious, and dissolves much more readily in water, forming an intensely acid solution. It forms the normal hydrate $As O_4 H_3$, from which all the water can gradually be expelled by the application of heat; lower hydrates being first formed. Arsenic acid cannot be volatilized without decomposition, for when sufficiently heated it breaks up into arsenious acid and oxygen. Its solution expels carbonic acid from sodic carbonate, forming the salt $As O_4 Na_2 H (H_2 O)_{12}$, isomorphous with common hydro-di-sodic phosphate. There is also a sodic arseniate containing three atoms of sodium ($As O_4 Na_3 (H_2 O)_{12}$), and another containing only one atom of sodium and two of basic hydrogen ($As O_4 Na H_2 (H_2 O)$), having a strongly acid reaction.

Arsenic acid is easily distinguished from arsenious acid by the red-brown colour of the argentic arseniate $As O_4 Ag_3$. An acid solution of an arseniate is very slowly reduced by sulphuretted hydrogen with deposition of sulphur—

$$As O_4 H_3 + H_2 S = As O_3 H_3 + S + H_2 O.$$

The arsenious acid thus formed is subsequently decomposed, forming arsenious sulphide, but the process is so extremely slow that arsenic acid is usually reduced by boiling with sulphurous acid prior to the action of sulphuretted hydrogen. Arsenic acid forms with magnesia and ammonia an important double salt, $As O_4 Mg N H_4 (H_2 O)_6$, which serves for the quantitative estimation of the acid. This salt loses none of its ammonia at the heat of the water-bath.

139. Arseniuretted Hydrogen ($As H_3$ = 2 vols.) is readily formed together with hydrogen when an arsenite is present in a mixture of dilute hydric sulphate and metallic zinc; $H_3 As O_3 + 3 H^2 = As H_3 + 3 H_2 O$. The process goes commonly by the name of Marsh's test. Arseniuretted hydrogen is a very poisonous gas, condensible by cold.

When hydrogen containing arseniuretted hydrogen is passed into a solution of argentic nitrate, a reduction of metallic silver takes place simultaneously with a formation of arsenious acid.

Arsenious Chloride ($As Cl_3 = 2$ vols.). Metallic arsenic burns in chlorine gas, forming this chloride, whatever may be the proportions of the materials employed. The compound is at the ordinary temperature a heavy liquid; it boils at 132°C. It combines with water, but in presence of a large quantity of water it is decomposed into hydric arsenite and hydric chloride—

$$As Cl_3 + 3 H_2 O = H_3 As O_3 + 3 H Cl.$$

When arsenious acid or one of its salts is distilled with hydric chloride of at least 1.1 density, arsenious chloride passes over with the aqueous acid; and the reaction affords an excellent means of separating arsenic from organic or other bodies which would interfere with its other reactions.

Arsenic forms a tribromide which is solid at the ordinary temperature. Also a corresponding iodide which is obtained in the form of red crystals.

140. Three **Sulphides of Arsenic** are known—namely, a red bisulphide ($As_2 S_2$) commonly called realgar; a yellow tersulphide (arsenious sulphide—As_2S_3); and a pentasulphide (arsenic sulphide), which is also yellow.

Arsenious sulphide is readily obtained by passing sulphuretted hydrogen through a solution of arsenious acid, containing free hydric chloride. It is insoluble in hydric chloride but dissolves in ammonic sulphide, forming ammonic sulpharsenite ($As S_3 (N H_4)_3$).

Acid hydrogen salts readily decompose the solution of this salt, precipitating arsenious sulphide and liberating sulphuretted hydrogen—

$$2 As S_3 (N H_4)_3 + 6 H Cl = As_2 S_3 + 3 H_2 S + 6 N H_4 Cl.$$

Arsenic sulphide dissolves readily in caustic alkalies, and it even dissolves, though less readily, in ammonic carbonate.

It evaporates unchanged when heated without access of air.

Arsenic sulphide can be obtained by passing sulphuretted hydrogen into a solution of sodic arseniate as long as any of the gas is absorbed. The oxygen of the salt is thus replaced by sulphur—

$$As O_4 Na_2 H + 4 H_2 S = As S_4 Na_2 H + 4 H_2 O.$$

The solution of the sulpharseniate is then decomposed by hydric chloride—

$$2 As S_4 Na_2 H + 4 H Cl = As_2 S_5 + 3 H_2 S + 4 Na Cl.$$

CHAPTER XXII.

141. Antimony (Sb=122) is a very brittle crystalline metal, having a density of 6.7. It is far less volatile than arsenic, requiring a bright red heat for its volatilization, and its vapour burns in the air with a brilliant white flame.

The metal is not attacked by hydric chloride. Hydric nitrate converts it into a white oxide insoluble in that liquid.

Strong hydric sulphate dissolves it with the aid of heat evolving sulphurous acid—

$$Sb^2 + 6\,H_2\,S\,O_4 = Sb_2\,(S\,O_4)_3 + 6\,H_2\,O + 3\,S\,O_2.$$

The metal can be obtained by the action of hydrogen at a red heat upon either antimonious acid or the antimonious sulphide. It is commonly prepared on a large scale by heating antimonious sulphide with metallic iron—

$$Sb_2\,S_3 + Fe_3 = Sb^2 + 3\,Fe\,S.$$

Antimony combines in two proportions with oxygen, forming antimonious acid, sometimes called antimonic oxide, and antimonic acid.

142. Antimonious Acid ($Sb_2\,O_3$) is obtained by decomposing antimonious chloride by water. The last portions of the hydric chloride are best removed by the aid of a solution of sodic carbonate. The white powder is deprived of its water by the aid of heat. At a high temperature antimonious acid melts, and it can be volatilized with difficulty. It is dissolved by a solution of hydro-potassic tartrate, forming the well-known salt tartar emetic; and in this salt the

oxide does not shew the property which belongs to the chloride—of undergoing precipitation by water.

Antimonious acid dissolves in caustic potash. It reduces metallic silver from argentic nitrate neutralized by ammonia.

Antimonic Acid ($Sb_2 O_5$) is formed by the action of liquid nitrates such as hydric nitrate on metallic antimony. It is a white powder, almost insoluble in water, and soluble with difficulty in hydric chloride.

When strongly heated it gives off one-fifth of its oxygen, leaving a compound of two atoms of antimony with four atoms of oxygen ($Sb^2 O_4$), which may be regarded as consisting of antimonic acid combined with antimonious acid.

Antimonic acid is remarkable for forming with soda a salt nearly insoluble in water, and quite insoluble in dilute alcohol. This salt is called sodic antimoniate ($Na_3 Sb O_4$).

143. Antimoniuretted Hydrogen ($Sb H_3$) is formed in a similar manner to arseniuretted hydrogen, and resembles that compound greatly in its properties. It is decomposed by passing through a glass tube of small diameter heated by a gas-flame, and a ring of bright metallic antimony is deposited from it. The ring of antimony thus obtained can be distinguished from the ring of arsenic, obtained in a similar manner from arseniuretted hydrogen, by the lesser volatility of the antimony, and also by the circumstance that the antimonious acid formed by heating the metal in contact with air does not (like arsenious acid) dissolve in water.

When antimoniuretted hydrogen is passed into a solution of argentic nitrate, a precipitate of argentic antimonide is formed: thus,

$$Sb H_3 + 3 Ag N O_3 = Sb Ag_3 + 3 H N O_3.$$

A boiling solution of hydric tartrate takes up antimonious acid from this precipitate, no doubt with the intervention of atmospheric oxygen.

Antimony combines in two proportions with chlorine—

forming a trichloride (antimonious chloride) and a pentachloride (antimonic chloride).

144. Antimonious Chloride ($SbCl_3$ = 2 vols.) is most readily prepared by dissolving lumps of antimonious sulphide in strong hydric chloride with the aid of heat—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The solution thus obtained is evaporated to dryness (some antimonious chloride escaping during the process), and the antimonious chloride is purified by distillation. In this manner it is obtained in the form of a white crystalline mass.

Water decomposes the antimonious chloride, forming hydric chloride, and a basic chloride; and the chloride formed by the decomposition of one part of the salt dissolves some of it. Water acts in a similar manner on a solution of the chloride in hydric chloride, for when a saturated solution of antimonious chloride in concentrated hydric chloride is diluted with water, some of the antimony is precipitated as a basic salt, the remainder being held in solution by the more dilute chloride.

Antimonic Chloride ($SbCl_5$) is formed by passing dry chlorine into a vessel containing the trichloride. It is a heavy yellow liquid, and emits dense fumes in contact with moist air. Antimonic chloride is decomposed by heat, chlorine gas making its escape in abundance, and carrying some of the chloride with it. The vapour formed from this body has a density corresponding to $SbCl_5$ = 4 vols.; and the fact of the liberation of free chlorine with the formation of the lower chloride, is a strong argument in favour of a similar explanation of the anomalous vapour-density of phosphoric chloride.

145. Antimonious Sulphide (Sb_2S_3) is formed by the action of sulphuretted hydrogen on a solution of the oxide in an acid hydrogen salt, provided there be not a great excess of the acid salt present.

It is an orange-coloured precipitate, but after fusion it is much darker in colour, and the black native sulphide is the most abundant ore of antimony.

Antimonious sulphide dissolves readily in ammonic sulphide, but, unlike arsenious sulphide, it does not dissolve in ammonic carbonate (carbonate of ammonia).

Antimonic sulphide (Sb_2S_5) is very similar to the lower sulphide in its appearance and properties. It forms crystallizable salts with sulphur bases, such as the sodic sulph-antimoniate, $SbS_4Na_3(H_2O)_9$.

CHAPTER XXIII.

146. Tin (Sn = 118) is prepared chiefly from its binoxide called tinstone, from which it is easily reduced by being heated in contact with coal. It melts at 228°C. Although crystalline in its structure, a mass of metallic tin cannot, like antimony, be reduced to powder in a mortar. The effect of hammering it is to flatten and extend the mass. Tin can even be rolled into thin foil or drawn into wire. Although it melts at a low temperature, it cannot be volatilized without great difficulty. When kept in the fluid state in contact with air, it gradually absorbs oxygen, forming the binoxide $Sn O_2$.

Hydric chloride dissolves tin with the aid of heat, forming stannous chloride—

$$2 H Cl + Sn = Sn Cl_2 + H^2.$$

Hydric nitrate acts upon tin in the same sort of way as upon antimony, converting it into a white oxide insoluble in that liquid.

147. Tin forms two definite oxides—the **Stannous Oxide** Sn O, which is a strong base, and the **Stannic Oxide** $Sn O_2$, commonly called stannic acid, which has feebler basic properties, and willingly acts the part of an acid.

Stannous Oxide (Sn O) may be prepared by adding ammonia to a solution of stannous chloride, and then boiling the precipitate produced with excess of ammonia. Stannous oxide easily combines with another atom of oxygen, being converted into the higher oxide, and for this reason stan-

nous salts are powerful reducing agents. Caustic potash precipitates stannous oxide in combination with water from a solution of stannous chloride, and an excess of potash dissolves it. If the solution thus obtained be boiled, metallic tin is deposited, and potassic stannate formed. In this case one molecule of stannous oxide is oxidized at the expense of a second—

$$2\,Sn\,O + 2\,K\,H\,O = Sn + K_2\,Sn\,O_3 + H_2\,O.$$

Stannic Acid is remarkable for the different properties which it manifests according to the manner in which it is prepared. When formed by oxidation of tin by hydric nitrate it is insoluble in hydric chloride, but when prepared by the precipitation of a solution of stannic chloride by a carbonate it is readily soluble in hydric chloride. The soluble kind becomes insoluble by heat, and on the other hand, the insoluble variety can be rendered soluble by fusion with caustic potash.

Hydric tartrate scarcely dissolves the stannic oxide formed by the nitrate, and affords in this manner a convenient distinction between tin and antimony.

148. Stannous Chloride ($Sn\,Cl_2$) is usually prepared in combination with water by dissolving the metal in hydric chloride. The crystals which are deposited from the solution after concentration, contain two molecules of water of crystallization ($Sn\,Cl_2\,(H_2\,O)_2$). They are decomposed by water in the same sort of way as antimonious chloride, though to a lesser degree. The water cannot be expelled from these crystals by heat without carrying away hydric chloride. Stannous chloride absorbs oxygen readily, and is a powerful reducing agent. If stannous chloride be poured gradually into a solution of mercuric chloride, a white precipitate of mercurous chloride is formed—

$$2\,Hg\,Cl_2 + Sn\,Cl_2 = Sn\,Cl_4 + Hg^2\,Cl_2,$$

and if more stannous chloride be added, the mercury is deposited in the metallic state—

$$Hg^2 Cl_2 + Sn Cl_2 = Sn Cl_4 + 2 Hg.$$

When mixed with a solution of auric chloride it causes the appearance of a deep brown colour; and if sufficient quantity of the materials be used, a precipitate of Cassian purple is formed.

149. Stannic Chloride ($Sn Cl_4 = 2$ vols.). This volatile liquid was formerly known by the name of fuming spirit of Libavius. It is most easily prepared by distilling granulated tin with about four times its weight of mercuric chloride, care being taken to exclude moisture. It combines with a small quantity of water, forming crystals of a hydrate. A large quantity of water decomposes its solution partially into hydric chloride, which dissolves, and gelatinous flakes of stannic hydrate.

By the prolonged action of metallic iron, a solution of stannic chloride is reduced to the state of stannous chloride, but no further; if zinc be used the tin will be reduced to the metallic state. This constitutes an important distinction from arsenic and antimony, both of which are reduced to the metallic state by either iron or zinc.

150. Stannous Sulphide ($Sn S$) is a dark brown precipitate obtained by passing sulphuretted hydrogen into a solution of stannous chloride. It is dissolved by yellow ammonic sulphide, being converted into stannic sulphide by combining with free sulphur contained in that reagent. This is shown by the precipitation of the yellow stannic sulphide on the addition of hydric chloride.

Stannic sulphide ($Sn S_2$) differs from arsenious sulphide by its lesser solubility in ammonic carbonate, and from antimonious sulphide by its insolubility in hydric chloride.

151. The rare metal **Titanium** ($Ti = 50$) has in its compounds considerable analogy with tin. It occurs in nature

as titanic acid, TiO_2, of which three varieties are known, differing in crystalline form and in specific gravity. Titanic acid as thus found is insoluble in all acid salts except hydric fluoride and boiling hydric sulphate, but it may be rendered soluble in cold hydric chloride by fusion with potassic carbonate. From this acid solution titanic acid is precipitated on boiling. Copper-coloured cubic crystals are occasionally found in certain iron furnaces, and these crystals were for a long time supposed to be metallic titanium, but they were afterwards shown to be composed of carbon, nitrogen, and titanium.

Titanic Chloride ($TiCl_4$) is obtained by passing a current of dry chlorine over a mixture of titanic acid and charcoal heated to redness.

Tungsten and molybdenum constitute a natural family of metals, and the compounds of the first of them are already coming into use.

152. Tungsten (W = 184). Tungsten is found as a mangano-ferrous tungstate in the mineral Wolfram, which accompanies tin-ore, and from its high specific gravity cannot be separated from it by washing. The metal can be reduced by charcoal or hydrogen from one of its oxides, at a high temperature. It is very difficult of fusion; density 17.6.

Tungsten forms a peroxide, and a trioxide (WO_3) called tungstic acid.

Tungstic acid is insoluble in water and in hydric chloride. Its normal soda salt ($WO_4Na_2(H_2O)_2$) is prepared for impregnating cambric, and thereby rendering it uninflammable. Nascent hydrogen gradually desoxidizes tungstic acid, forming tungstic peroxide. But by carefully regulating the action it is easy to arrest the reduction half way, leaving a deep indigo-blue oxide.

Tungsten forms a bisulphide, and a trisulphide which

combines with the alkaline sulphides, forming soluble sulphur salts.

153. Molybdenum ($Mo = 96$) is found in nature in combination with sulphur. When this sulphide ($Mo S_2$) is heated in contact with air, sulphurous acid is formed and escapes in the gaseous state, while molybdic acid ($Mo O_3$) remains behind. Molybdic acid dissolves in ammonia, and the solution is precipitated by the cautious addition of hydric nitrate, but an excess of that body easily redissolves the precipitate. The solution thus obtained forms with a soluble phosphate a very insoluble precipitate, and is used as a test for minute traces of that body.

Molybdic sulphide forms sulphur salts with alkaline sulphides.

154. Gold ($Au = 196.5$) is classed among the **noble metals** in virtue of its having no tendency to rust, and because most of its compounds decompose spontaneously at a high temperature. It is one of the heaviest of metals, its density varying from 19.2 to 19.4. It melts at about 1100°C. It is a very soft metal, and can be hammered out to a leaf so thin as to be transparent, allowing green rays of light to pass through it.

Gold is not dissolved by acid nitrates, chlorides, or sulphates, even on boiling. Its commonest solvent is a mixture of strong hydric chloride and nitrate, called aqua regia. The yellow solution obtained by aqua regia consists of auric chloride ($Au Cl_3$). The metal is precipitated from this solution completely, in the form of a soft brown powder, by ferrous sulphate—

$$3\,Fe S O_4 + Au Cl_3 = Fe Cl_3 + Fe^2 (S O_4)_3 + Au.$$

It can also be reduced by oxalates.

At the melting-point of tin, auric chloride loses two atoms of chlorine, being reduced to aurous chloride ($Au^2 Cl_2$). The auric oxide, corresponding to the trichloride, is fre-

quently called auric acid. In the free state its composition is represented by the formula Au_2O_3. Potassic aurate ($Au O_2 K (H_2 O)_3$) is a crystallizable salt.

Auric chloride might with equal right be called chlorauric acid, for it combines with potassic chloride, sodic chloride, &c., forming crystallizable salts: e. g. $Au Cl_4 Na (H_2 O)_2$.

Sulphuretted hydrogen precipitates gold from its acid solutions as a dark brown sulphide.

155. Platinum (Pt=197; density 21.5) is another noble metal. In compact masses it is white, but it can be obtained by precipitation in the form of a black powder like lampblack. The metal requires for its fusion the temperature of a flame fed with oxygen. Platinum possesses the valuable property of uniting when two masses of it are pressed or hammered together at a high temperature. The operation of uniting two or more masses of metal into one in this manner is called 'welding.'

The original process of working platinum was devised by Dr. Wollaston. The ore, which consists of white metallic particles, containing platinum combined with some other metals, is purified by boiling with hydric nitrate, and then with hydric chloride. It is then warmed with strong chloride, with occasional additions of the nitrate. The solution containing platinic chloride is diluted, and precipitated by a solution of ammonic chloride. The precipitate is a yellow double salt, consisting of platinic chloride combined with ammonic chloride ($Pt Cl_6 (N H_4)_2$). This ammonio-platinic chloride is collected and heated to redness, everything but platinum going off, and the platinum being left in a spongy form. This spongy platinum is heated, compressed, and hammered until it is brought down to a coherent mass of 21.5 density. A new plan has been lately brought into operation by Deville and Debray, whereby liquid metallic lead is made to dissolve out the platinum from its ore, whilst

the impurities are left undissolved. The lead is subsequently burnt away from the alloy of lead and platinum, and the platinum is finally melted in a crucible of lime by a flame fed with oxygen.

Platinum is one of the most tenacious of metals, and is valuable as a material for the manufacture of vessels in which strong acids or fluorides have to be heated. It is oxidized by fusion with potash or soda in contact with air. It also combines readily with metals and with phosphorus at a high temperature. The metal forms two oxides—viz. platinous oxide (PtO) and platinic oxide (PtO_2), both of which are bases; but the platinic oxide has almost equal claims to be classed among acids, as it combines with strong bases.

Both oxides give off all their oxygen at a high temperature. There are two sulphides corresponding in composition to the two oxides. Platinic sulphide dissolves somewhat in alkaline sulphides.

156. The ordinary solution of platinum is a tetrachloride, or rather a compound of the tetrachloride with hydric chloride ($PtCl_6H_2$).

When its solution is evaporated to dryness and carefully heated to about 230°C, it gives off hydric chloride and half its remaining chlorine, leaving platinous chloride ($PtCl_2$), a dark green powder insoluble in water. This platinous chloride is decomposed in its turn by still stronger heat. Solutions of platinum are not, like those of gold, reduced by ferrous sulphate, nor by oxalates. Formiates reduce platinum with the aid of heat when present in a neutral solution.

The action of ammonia on platinous chloride gives rise to the formation of bases, which consist of ammonia in which a part of the hydrogen is replaced by platinum. In illustration of these remarkable bodies may be mentioned the compound $PtCl_2N_4H_{12}$, which is formed by dissolving

platinous chloride in ammonia and crystallizing the solution. It is considered to be a compound of hydric chloride with a kind of ammonia, consisting of $N_4\,H_{10}\,Pt$. By heating the salt, ammonia can be easily expelled, and the compound $Pt\,Cl_2\,N_2\,H_6$ is obtained.

CHAPTER XXIV.

157. Silver (Ag = 108; sp. gr. = 10.5; melting-point, 1023°). This most beautiful metal is sometimes found in the pure state as so-called native silver. It also occurs with other metals, in combination with sulphur, and among ores of this kind galena is the most plentiful. This mineral consists mainly of plumbic sulphide, but the metallic lead prepared from nearly all samples of it contains a small quantity of silver. Although the quantity of silver frequently amounts only to a few ounces in the ton of lead, it is profitably extracted by **Pattinson's** admirable **process**. This process consists in melting the argentiferous lead in large iron pots, and allowing the molten mass to cool gradually. Crystals soon make their appearance in the mass, and these are removed by iron strainers as fast as they appear, until the greater part of the contents of the pot have been removed in the form of crystals. These crystals are melted in a second pot, and separated by a second crystallization while they are cooling, and the process is repeated until at last crystals are obtained containing only about half an ounce of silver in the ton, while the greater part of the silver is collected in those portions of lead which were left in the pots after the removal of the crystals of lead. The final purification of the silver is by so-called **cupellation,** which is a process of burning away the metallic lead in a shallow vessel called a cupel, heated by oxidizing flames which are made to play over its surface. The silver is left free from lead;

and copper, if present in small quantity, is removed by the plumbic oxide.

Silver possesses the remarkable property of absorbing oxygen from the air while it is liquid, and giving the gas off again while it is solidifying. When a mass of molten silver is allowed to cool, the film of solid metal which is formed upon its surface is raised and burst in several places by the escaping oxygen. This phenomenon is called spitting, and a loss of silver is very liable to occur during cooling.

Standard silver is an alloy containing 7.5 per cent. of copper to 92.5 of silver.

158. Silver is readily dissolved by hydric nitrate, and with the aid of heat, in strong sulphate. Hydric chloride has scarcely any action upon it.

It forms with oxygen the strong base argentic oxide Ag_2O, and the neutral peroxide Ag_2O^2. There is also some reason to believe in the existence of a suboxide Ag_4O. These oxides are completely decomposed by heat.

Argentic oxide can be obtained by cautiously heating argentic nitrate. Caustic potash added to a solution of the nitrate precipitates the hydrate AgHO. Ammonia produces a similar effect, but an excess of ammonia readily dissolves the hydrate.

Argentic Oxide is remarkable among bases for forming anhydrous salts, and a silver salt is the best one to prepare and analyze, whenever the equivalent weight of an acid salt has to be determined with the utmost trustworthiness. By the action of light, silver is readily reduced to the metallic state from its salts, if any oxidizable matter be present. Formiates reduce it rapidly with the aid of heat, in neutral solutions, in the form of a light grey powder. Sulphites act in a similar manner.

Argentic nitrate (NO_3Ag), or 'lunar caustic,' is one of the most important salts of the metal. It crystallizes in

plates which contain no water. The salt dissolves in about its own weight of water at 15°C. When heated it melts to a clear liquid, and does not decompose until heated to a higher temperature.

Silver forms a white oxalate, insoluble in water but soluble in hydric nitrate.

Argentic carbonate is a yellowish salt easily obtained by precipitating a solution of a salt of silver by a soluble carbonate. It is insoluble in water but readily dissolved by hydric nitrate. Its composition is represented by the formula $C O_3 Ag_2$.

Argentic cyanide (C N Ag) is obtained as an amorphous white precipitate, when prussic acid is added to a solution of argentic nitrate. It is not dissolved by hydric nitrate in the cold, but dissolves on boiling. Ammonia dissolves argentic cyanide. It is decomposed by heat.

159. Argentic Chloride (Ag Cl) is a salt which is quite insoluble in water. It is thrown down in the form of a curdy white precipitate, devoid of all crystalline structure, when argentic nitrate is mixed with a soluble chloride, such as hydric or sodic chloride—

$$N O_3 Ag + Cl Na = Cl Ag + N O_3 Na.$$

It is not dissolved by hydric nitrate even on boiling, but is readily dissolved by ammonia. When heated strongly by itself argentic chloride melts, and on cooling has the appearance of horn, from which circumstance it has been named horn-silver. Its chlorine is carried away by volatile hydrocarbons, at a high temperature; and metallic silver is easily obtained from the chloride by melting it with sodic carbonate, when oxygen and carbonic acid are given off.

When argentic chloride is moistened with dilute hydric sulphate, and a piece of metallic zinc is immersed in the liquid and made to touch the chloride, a gradual transfer of the chlorine from the silver to the zinc takes place, first at the

spot at which the zinc touches the chloride, and from that onwards through the whole mass, $2\,AgCl + Zn = Ag^2 + ZnCl_2$.

Argentic chloride is readily dissolved by sodic hyposulphite; also by potassic cyanide.

A saturated solution of sodic chloride dissolves an appreciable quantity of argentic chloride, but the whole of the argentic chloride is precipitated when the solution is sufficiently diluted.

Argentic chloride is darkened by exposure to sunshine, the change of colour being accompanied by a loss of chlorine.

Argentic bromide is a salt much like the chloride. It is, however, less soluble in ammonia than the chloride, as can be seen by adding a solution of potassic bromide to ammonia saturated by argentic chloride.

Argentic iodide is a yellow salt, distinguishable from the chloride and bromide by being insoluble in ammonia. It can be formed from a mixture of potassic chloride and iodide by adding argentic nitrate in quantity not sufficient to precipitate all the iodine in the solution.

160. Argentic Sulphide (Ag_2S) is a black compound which occurs in the mineral kingdom crystallized in octohedra similar to those formed by cuprous sulphide (Cu^2S). It is precipitated by the addition of sulphuretted hydrogen or ammonic sulphide to a solution containing silver, and it does not dissolve in an excess of ammonic sulphide.

Argentic sulphide is oxidized by hydric nitrate, the silver being dissolved as argentic nitrate, and the sulphur forming hydric sulphate.

Argentic Sulphate (SO_4Ag_2) is a salt which dissolves very sparingly in water, and crystallizes in a similar form to anhydrous sodic sulphate (SO_4Na_2).

Argentic sulphite (Ag_2SO_3) is obtained as a white precipitate by adding an aqueous solution of sulphurous acid to argentic nitrate. It is not easily soluble in hydric nitrate.

Hydric borate forms a white silver salt, but like other borates this salt is dissolved by neutral saline solutions.

Hydric phosphate forms a bright yellow silver salt, containing three atoms of silver in its molecule. The reaction between hydro-di-sodic phosphate and argentic nitrate consists in an interchange between three atoms of silver on the one hand, and two of sodium plus one of hydrogen on the other hand—

$$P O_4 Na_2 H + 3 Ag N O_3 = P O_4 Ag_3 + 2 Na N O_3 + N O_3 H.$$

The argentic phosphate dissolves readily in hydric nitrate, or in ammonia.

CHAPTER XXV.

161. Mercury (Hg = 200; density 13.5; Hg = 2 vols.; vapour density 100; melting point −39.5; boiling point 357). This metal is sometimes found native in the form of globules dispersed through rocks, but more frequently as cinnabar, which is mercuric sulphide. Its extraction is a very simple process. A mixture of cinnabar with quick-lime is distilled in a cast-iron retort, and the vapour of mercury which passes off from the mixture is led into a receiver containing water—

$$4\,Hg\,S + 4\,Ca\,O = 4\,Hg + 3\,Ca\,S + Ca\,S\,O_4.$$

Commercial mercury frequently contains lead, or some other foreign metal dissolved in it; and the presence of any considerable amount of impurity of the kind can be discovered by pouring a few drops of the mercury upon a dry plate, and then inclining the plate so as to make the metal run about on it. Pure mercury leaves no mark on the plate, but a thin metallic streak (called a tail) is left by impure mercury. In colour it approaches nearly to silver, and in one class of its compounds it possesses some analogy with that metal. It is, however, a di-valent metal, and has a great tendency to form basic salts, as well as double salts, in which two different atoms of acid radical are combined with one atom of the metal. Hydric chloride has no action upon it. Strong hydric sulphate is decomposed by it with the aid of heat, forming mercuric sulphate and sulphurous acid.

Dilute hydric nitrate dissolves the metal readily; but the

compound formed by the action of a small quantity of the nitrate, insufficient to dissolve all the mercury, is mercurous nitrate ($Hg^2(NO_3)_2$), whereas the action of an excess of nitrate forms mercuric nitrate ($Hg(NO_3)_2$). Mercury forms two compounds with oxygen, both of which are bases.

162. Mercurous oxide (Hg^2O) can be obtained by the action of potash on calomel or mercurous nitrate. It is a dark grey powder, but is decomposed readily by heat into free metallic mercury, and red mercuric oxide—

$$Hg^2O = Hg + HgO.$$

The oxygen in mercurous oxide,

$$Hg^2O + 2HCl = Hg^2Cl_2 + H_2O,$$

can be replaced by two atoms of chlorine, or of bromine, or iodine; or by two atoms of the monovalent salt radical NO_3. In like manner it can be replaced by one atom of sulphur. These compounds are called subsalts of mercury, or mercurous salts.

Red Oxide of mercury, or mercuric oxide, is formed by boiling the metal for a long time in contact with air; but a far more convenient way of preparing the oxide is to heat mercuric nitrate slowly and cautiously as long as any red fumes come off from it. Too strong a heat would decompose the oxide, driving off oxygen and metallic mercury.

When potash is added to a solution of mercuric nitrate or chloride, the oxide is thrown down in the form of a bright yellow powder. This peculiar colour is due to the finely-divided state in which the particles are then precipitated, and the common red oxide becomes yellower the more finely it is powdered.

Both oxides of mercury are remarkable for the facility with which they form basic salts.

Mercurous Nitrate is best prepared by warming hydric nitrate, diluted with four times its volume of water, with an excess of metallic mercury, pouring the solution off from the

residual metal, and crystallizing it after the addition of some more hydric nitrate. The crystals contain

$$(Hg\,N\,O_3)_2\,(H_2\,O)_3.$$

By the action of water this salt is decomposed, forming a yellow double salt, called mercurous hydro-nitrate—

$$(Hg\,N\,O_3)_2\,(H_2\,O)_3 + n\,H_2\,O = Hg^2\,N\,O_3\,H\,O + \\ + N\,O_3\,H + (n+2)\,H_2\,O.$$

There is also a soluble mercurous hydro-trinitrate, having a composition represented by the formula $Hg_4\,(N\,O_3)_3\,H\,O$.

Mercuric Nitrate ($Hg\,(N\,O_3)_2$) is obtained by boiling the metal with hydric nitrate until a sample of the solution, diluted with water, gives no precipitate with a soluble chloride. The solution when freed by evaporation from excess of the acid salt, deposits, on cooling, crystals of mercuric hydro-nitrate $Hg\,N\,O_3\,H\,O$, and these in their turn are readily decomposed by water, with formation of a more basic salt of yellow colour.

Mercuric Cyanide ($Hg\,(C\,N)_2$) is a salt of considerable stability, for it is not decomposed by a solution of potash. Prussic acid dissolves mercuric oxide readily, and forms, with an excess of the oxide, a soluble basic cyanide which has an alkaline reaction to test-paper. Prussic acid, added to a solution of mercurous nitrate, forms mercuric cyanide, and precipitates metallic mercury—

$$2\,H\,C\,N + Hg^2\,(N\,O_3)_2 = Hg\,(C\,N)_2 + Hg + 2\,H\,N\,O_3.$$

163. Mercurous Chloride ($Hg^2\,Cl_2 = 4$ vols.; vapour density $= 117.75$), generally called calomel, is obtained by precipitating mercurous nitrate by a solution of common salt—

$$Hg^2\,(N\,O_3)_2 + 2\,Na\,Cl = Hg^2\,Cl_2 + 2\,Na\,N\,O_3.$$

It is also formed by the action of reducing agents, such as a sulphite, on a mixture of common salt with a soluble mercuric salt—

$$2\,Hg\,(N\,O_3)_2 + H_2\,S\,O_3 + 2\,Na\,Cl + H_2\,O = Hg^2\,Cl_2 + \\ + Na_2\,S\,O_4 + 4\,H\,N\,O_3.$$

It is easily prepared on a large scale by heating together a mixture of mercuric sulphate, metallic mercury, and common salt—

$$Hg S O_4 + Hg + 2 Na Cl = Hg^2 Cl_2 + S O_4 Na_2.$$

Calomel is quite insoluble in water, but it sometimes contains corrosive sublimate, which can easily be detected by its solubility in water. Calomel is decomposed by boiling with hydric chloride into mercuric chloride and free metallic mercury. The same action is exerted, though more slowly, by other soluble chlorides.

It does not dissolve in dilute hydric nitrate in the cold.

Ammonia blackens it, dissolving out half of its chlorine, and replacing the chlorine so removed by amidogen ($N H_2$)—

$$Hg^2 Cl_2 + 2 N H_3 = Hg^2 Cl N H_2 + N H_4 Cl.$$

164. Mercuric Chloride, or corrosive sublimate ($Hg Cl_2$ = 2 vols.; sp. gr. of vapour 135·5), can be obtained by dissolving mercuric oxide in hydric chloride, or by subliming a mixture of salt and mercuric sulphate—

$$2 Na Cl + Hg S O_4 = Cl_2 Hg + S O_4 Na_2.$$

Corrosive sublimate dissolves in water, and still more readily in alcohol.

Sulphuretted hydrogen, passed gradually into its solution, gives at first a brown precipitate, which becomes white by agitation with an excess of the chloride. The white precipitate is a mercuric sulphochloride $Hg_2 Cl_2 S$. An excess of sulphuretted hydrogen converts this white precipitate into black sulphide.

Ammonia added in excess to a solution of mercuric chloride forms a white precipitate, which is used in medicine by the name of 'white precipitate.' The action is perfectly similar to that between calomel and ammonia, viz. an interchange of $N H_2$ and Cl—

$$Hg Cl_2 + 2 N H_3 = Hg N H_2 Cl + N H_4 Cl.$$

This white precipitate is soluble in nitrate or in chloride.

Potash precipitates yellow mercuric oxide from a solution of chloride, and potassic carbonate forms a somewhat darker precipitate, containing scarcely any carbonic acid.

Corrosive sublimate is precipitated by albumen, and this substance is accordingly administered as an antidote in all cases of suspected poisoning by the sublimate.

A solution of corrosive sublimate is decomposed by metallic copper, the mercury being deposited upon the surface of the copper in the form of a grey coating, which shews the metallic lustre of mercury after rubbing—

$$Hg\,Cl_2 + Cu = Hg + Cu\,Cl_2.$$

Mercurous iodide is an olive-green precipitate decomposable, by an excess of potassic iodide, into red mercuric iodide, which dissolves, and grey metallic mercury, which remains undissolved.

Mercuric Iodide is precipitated in the form of a brilliant scarlet powder, when mercuric chloride is mixed with potassic iodide. The precipitate dissolves in excess of either reagent. It fuses when strongly heated, and then evaporates, but the crystals which are formed by the condensation of its vapour are of a bright yellow colour. When kept at the common atmospheric temperature these yellow crystals turn scarlet again.

165. Mercuric Sulphide, or cinnabar (Hg S), is the chief ore of mercury. It is prepared of a deep red colour by combining metallic mercury with sulphur dissolved in potassic sulphide. When formed by the action of an excess of sulphuretted hydrogen on a solution of mercuric salt it is black.

The black sulphide can be sublimed in a closed vessel, and it thereby acquires a red colour.

Mercuric sulphide is not attacked even by boiling hydric nitrate, but it is dissolved by aqua regia.

Mercurous sulphide is a black powder formed by the action of sulphuretted hydrogen on a mercurous salt.

Mercuric sulphate is a white crystalline salt, which is easily prepared by dissolving the metal in hot oil of vitriol. The salt is decomposed by water, leaving a bright yellow basic salt (called mineral turpeth) undissolved, while hydric sulphate is formed and dissolves some of the salts. The decomposition is represented by the equation

$$3\,Hg\,S\,O_4 + 2\,H_2\,O = Hg_3\,S\,O_6 + 2\,H_2\,S\,O_4.$$

Hydric phosphate forms with mercurous oxide a yellowish salt insoluble in water; and with mercuric oxide it forms a white salt insoluble in water, but soluble in acid salts, and even in sodic chloride.

CHAPTER XXVI.

166. Lead (Pb = 207; sp. gr. = 11.4, melting-point, 325°). This metal is so extremely soft, that it can be easily indented by the nail. It is made on a large scale by partially roasting galena, and then heating the residual ore with the plumbic oxide and sulphate which have been formed. In the first stage of the operation sulphurous acid is evolved while a mixture of plumbic oxide and plumbic sulphate is formed—

$$Pb\,S + 3\,O = Pb\,O + S\,O_2;\quad Pb\,S + 2\,O^2 = Pb\,S\,O_4.$$

In the second stage these products give up their oxygen and sulphur when heated with galena—

$$2\,Pb\,O + Pb\,S = 3\,Pb + S\,O_2;$$
$$Pb\,S\,O_4 + Pb\,S = Pb^2 + 2\,S\,O_2.$$

Lead is also obtained by heating galena with metallic iron—$Pb\,S + Fe = Pb + Fe\,S$.

Lead evaporates at a white heat, and its oxide is carried away easily by the gases in the flue during the reduction of the metal. The flues are in some lead-works constructed of great length, so as to collect this oxide as completely as possible.

Antimony and tin, when present in metallic lead, can in great part be removed by **refining**, which is a process of oxidizing the impurities in the lead by keeping the metal in a liquid state exposed to the action of air. Lead is oxidized at the same time, but less rapidly than those metals.

For laboratory purposes pure metallic lead is most easily obtained by fusing some plumbic acetate with crude hydro-potassic tartrate.

Lead expands greatly when heated, and does not on cooling always return to its original dimensions.

It is oxidized by moist air, and pure water containing oxygen dissolves plumbic oxide when placed in contact with the metal. For this reason leaden cisterns ought never to be used for collecting rain-water for domestic purposes.

167. Lead forms two definite oxides—the basic protoxide Pb O, called plumbic oxide, commercially called litharge, and the neutral binoxide $Pb O^2$.

Plumbic Oxide is best obtained in a pure state by boiling finely-powdered litharge with a solution of plumbic acetate. A basic salt is thus formed which has an alkaline reaction to litmus paper, and which readily absorbs free carbonic acid. The liquid should be filtered and carbonic acid passed through it. A white precipitate of plumbic hydro-carbonate ($Pb_3 (C O_3)_2 (H O)_2$) is thus formed. This precipitate can be collected on a filter, and the plumbic acetate which is reproduced can serve to make more hydro-carbonate. When a sufficient quantity of this salt has been thus prepared it is decomposed by cautious heating in a porcelain crucible, care being taken to expel all the carbonic acid and water, without melting the mass. A yellowish white oxide is thus obtained.

Plumbic oxide melts readily at a low red heat, and dissolves glass and earthenware, forming readily fusible plumbic silicates.

Plumbic oxide is pre-eminent for its tendency to form poly-acid salts. Thus it forms two oxy-hydrates,

$$Pb O Pb (H O)_2 \text{ and } (Pb O)_2 Pb (H O)_2,$$

but the normal hydrate $Pb O_2 H_2$ is not known.

It is dissolved readily by caustic potash, but very slightly by ammonia.

When plumbic oxide is cautiously heated in contact with air, it gradually absorbs oxygen and turns red. It is in this manner that **red lead** is prepared. The composition of red lead varies considerably in different samples, but they may all be considered as compounds of plumbic oxide with binoxide. The formula Pb_3O_4 represents an average composition. Hydric nitrate decomposes red lead, dissolving out plumbic oxide from it, and leaving brown binoxide undissolved—

$$Pb_3O_4 + 4\,HNO_3 = 2\,Pb(NO_3)_2 + PbO_2 + 2\,H_2O.$$

Plumbic Binoxide is decomposed by strong heat, with evolution of oxygen. When heated with strong hydric sulphate it forms plumbic sulphate, with evolution of oxygen. Hydric chloride decomposes it with the aid of heat, forming plumbic chloride and evolving chlorine—

$$PbO_2 + 4\,HCl = PbCl_2 + 2\,H_2O + Cl^2.$$

It absorbs sulphurous acid readily, forming plumbic sulphate.

168. Plumbic Nitrate (PbN_2O_6 or $Pb(NO_3)_2$) is a salt which crystallizes with facility from water. It has an acid reaction to test-paper. Its hot solution dissolves plumbic hydro-carbonate with effervescence, forming plumbic hydro-nitrate ($PbNO_3HO$).

Plumbic Carbonate ($PbCO_3$) is found native, and is called by mineralogists lead spar. It is formed in the cold by double decomposition between sodic carbonate and plumbic acetate. Two hydro-carbonates are also known. **White Lead**, or ceruse, consists usually of one of these compounds. It is made by exposing gratings of metallic lead to the simultaneous action of vinegar, air, and carbonic acid. Plumbic acetate is formed, and this takes up more plumbic oxide, forming the hydro-acetate, from which car-

bonic acid removes the hydrate, while the normal acetate thus reproduced dissolves more oxide for a second portion of carbonic acid to act upon. In this manner a continuous circle of decompositions takes place, and is allowed to continue until a thick crust of ceruse is formed over the surface of the lead, and the further action is retarded. This crust is then removed and ground up for use as white lead.

Plumbic Oxalate ($C^2 O_4 Pb$) is one of the most insoluble of lead salts in water, and when lead has to be precipitated from a solution, an oxalate is one of the best re-agents. The oxalate dissolves in hydric nitrate or chloride.

Plumbic Chloride ($Pb Cl_2$) is a salt which dissolves but slightly in cold water. It is obtained in the form of needle-shaped crystals by slowly cooling a solution saturated at a high temperature. It fuses at a moderate heat, and has the appearance of a horny mass after cooling.

Several basic plumbic chlorides are known. The compound $Pb^2 O Cl_2$ is prepared by Mr. Bell, of Newcastle, for use as a white paint. $Pb^3 O_2 Cl_2$ is found in the mineral kingdom, and known by the name of Mendipite. $Pb^4 O_3 Cl_2$ is obtained by heating the precipitate formed by ammonia in a solution of plumbic chloride. A still more basic compound is used as a yellow paint and called Cassel yellow.

Plumbic Iodide crystallizes from water in beautiful yellow scales.

169. Plumbic Sulphide, or galena ($Pb S$), is the chief ore of lead. Sulphuretted hydrogen precipitates this black sulphide even from the most dilute solutions of plumbic salts, and is the most delicate re-agent for detecting lead. Strong hydric chloride dissolves the sulphide, with evolution of sulphuretted hydrogen, but a small quantity of free chloride does not prevent the precipitation of a solution of lead by sulphuretted hydrogen.

Dilute nitrate dissolves out lead from the sulphide, leaving

the sulphur; and strong nitrate oxidizes both constituents, forming plumbic sulphate.

Plumbic sulphate ($Pb\,S\,O_4$) is a white salt, perfectly insoluble in water, but soluble in acid salts, in potash, and in many neutral salts, more especially in ammonic acetate or tartrate.

Plumbic sulphite ($Pb\,S\,O_3$) is very much like the sulphate in its properties.

Hydric phosphate forms a white normal salt with oxide of lead ($(P\,O_4)_2\,Pb_3$), soluble in hydric nitrate or chloride. There is also a double salt called pyromorphite, consisting of $(P\,O_4)_3\,Cl\,Pb_4$.

170. Bismuth (Bi = 210; sp. gr. = 9.8; melting-point, 266). This metal usually occurs native. It is exceedingly brittle, and its fracture exhibits bright crystalline surfaces of a reddish-white colour. It is easily oxidized by hydric nitrate, forming an oxide corresponding in constitution to antimonious oxide. Bismuth oxide ($Bi_2\,O_3$) dissolves in hydric nitrate, chloride, or sulphate, but the solutions thus obtained are decomposed by the addition of water, with precipitation of an oxysalt—

$$3\,Bi\,Cl_3 + 4\,H_2\,O = Bi_3\,O_2\,Cl_3\,(H\,O)_2 + 6\,H\,Cl.$$

Bismuth oxide can be prepared by heating metallic bismuth in contact with the air, or by deshydrating the precipitate formed by potash in a solution of a salt of bismuth. It is not soluble in potash or ammonia. Its salts are remarkable for the facility with which they exchange a part of their acid for water or oxygen, forming oxysalts and double salts. Thus bismuthic chloride gives a white precipitate, which after heating consists of bismuth oxychloride. The nitrate gives a precipitate of the composition $Bi\,N\,O_3\,(H\,O)_2$.

The normal bismuth nitrate $Bi\,(N\,O_3)_3(H_2\,O)_5$ is a crystallizable salt which dissolves in dilute nitrate. It gives off part of its hydric nitrate below 100°.

Bismuth chloride ($Bi\,Cl_3$) can be distilled, and has considerable resemblance to antimonious chloride.

Bismuth forms a compound corresponding to antimonic oxide. It is formed by passing chlorine through potash in which bismuth oxide is suspended.

In the anhydrous state bismuthic acid is represented by the formula $Bi_2\,O_5$. It forms a hydrate of the composition $Bi\,O_3\,H$.

Bismuth sulphide ($Bi_2\,S_3$) is a black compound, obtained by the action of sulphuretted hydrogen on acid solutions of the oxide.

CHAPTER XXVII.

171. Copper (Cu=63.5; sp. gr. 8.9). This important metal is occasionally found native. Its chief ore is **copper pyrites** (S_2 Cu Fe), which frequently occurs with iron pyrites.

The **smelting of copper** from pyrites is effected by a considerable number of operations.

A process of roasting, followed by fusion, serves to prepare a crude cuprous sulphide (called coarse metal), while the greater part of the iron is oxidized and dissolved in the slag as silicate. This coarse metal is granulated by letting it run in the molten state into water, and is then subjected to further oxidation by a process of 'roasting.' The mixture of oxides and sulphides of copper and iron thus obtained is melted together, and the cuprous sulphide which melts out of it is finally reduced to the metallic state by fusion in a reverberatory furnace, with limited supply of air. The upper portions are fully oxidized, forming sulphurous acid and cupric oxide; but this oxide gives off its oxygen to the remaining sulphide, forming sulphurous acid and metallic copper—

$$2\,Cu\,O + Cu^2\,S = 2\,Cu^2 + S\,O_2.$$

When copper is melted in contact with air it rapidly becomes converted into red oxide, and the liquid copper dissolves a portion of this oxide, thereby becoming brittle. The cuprous oxide is removed by stirring the liquid metal with a wooden pole, the charcoal and combustible gases

from which reduce the cuprous oxide to the metallic state. This operation is called poling.

Copper is sometimes obtained by the so-called process of **cementation,** which is a precipitation of copper from a dilute solution of cupric sulphate, by the action of metallic iron—

$$Fe + S O_4 Cu = S O_4 Fe + Cu.$$

Copper dissolves readily in hydric nitrate. Hydric chloride dissolves it with extreme slowness with the aid of heat; but if air have access to the acid surface of the metal, oxidation of the copper occurs, and a comparatively rapid solution takes place. Concentrated hydric sulphate dissolves the metal with the aid of heat, evolving sulphurous acid and water, and forming cupric sulphate and sulphide.

Aqueous ammonia in presence of air dissolves copper, forming a deep blue solution of the composition $Cu O (N H_3)_2$. A nitrite is formed at the same time. The metal acts very little on steam or carbonic acid even at a red heat. Copper forms two basic oxides, and a higher oxide possessing acid properties.

172. Cuprous Oxide ($Cu^2 O$) occurs as a mineral, and is called, from its form, octohedral copper ore. It can be prepared artificially by heating a solution of cupric hydrate in a mixture of potash and grape-sugar, from which it is precipitated as a red-brown powder. Cuprous oxide combines with acid salts, forming cuprous salts, which are for the most part insoluble in water but soluble in acid salts.

Cupric Oxide is a black substance obtained by heating metallic copper to redness in contact with the air. For some uses it is prepared by heating cupric nitrate to a red heat in an earthen crucible. If too strong heat be applied the oxide clots together, and ultimately even melts, giving off some of its oxygen. In analyses cupric oxide is prepared from a solution of one of its salts by adding caustic potash in excess,

and boiling the blue precipitate of cupric hydrate until it becomes black by losing its water.

Cupric oxide is reduced by hydrogen or carbonic oxide at a red heat.

Its salts are for the most part blue when combined with water, but they lose that colour when dried.

Copper combines with hydrogen, forming the compound called cuprous hydride ($Cu^2 H_2$). It is obtained by the spontaneous decomposition of a solution of cupric hypo-phosphite. Hydric chloride dissolves the hydride, with evolution of hydrogen, and with formation of cuprous chloride—

$$Cu^2 H_2 + 2\,H\,Cl = Cu^2 Cl_2 + 2\,H^2.$$

Two cupric hydro-carbonates are known. When a salt of copper is decomposed by sodic carbonate in the cold the precipitate is a hydro-carbonate, and carbonic acid is set free.

Blue copper ore ($Cu_3 (C O_3)_2 (H O)_2$) is a mineral which occurs in beautiful crystals.

Malachite is found in green masses, which are cut and polished for use as ornaments. Its composition is represented by the formula—

$$Cu_2 (C O_3) (H O)_2.$$

Cupric oxalate is obtained as a white precipitate, soluble in acids.

Cupric cyanide is formed by precipitating a solution of cupric sulphate by potassic cyanide. The cyanide dissolves in an excess of potassic cyanide, but undergoes a reduction to cuprous cyanide ($Cu^2 C_2 N_2$) during the process. This solution of cuprous cyanide is not decomposed by sulphuretted hydrogen.

Cupric Nitrate ($Cu (N O_3)_2$). This salt is formed by dissolving metallic copper in hydric nitrate. It is very soluble and crystallizes, sometimes with three molecules of water,

sometimes with six molecules. It cannot be dried without decomposition.

There are two chlorides of copper—a white cuprous chloride ($Cu^2 Cl_2$), which dissolves in hydric chloride, and a cupric chloride, which crystallizes from water in needle-shaped crystals of the composition $Cu Cl_2 (H_2 O)_2$.

With iodine copper forms only one compound, viz. cuprous iodide $Cu^2 I_2$; and when cupric sulphate is mixed with potassic iodide this salt is precipitated, while iodine is liberated at the same time—

$$2 Cu S O_4 + 4 K I = Cu^2 I_2 + I^2 + 2 K_2 S O_4.$$

Cupric sulphide is easily and completely thrown down as a black precipitate by the action of sulphuretted hydrogen on an acid solution of a salt of copper. There is also a cuprous sulphide $Cu^2 S$, which is formed during the process of smelting.

Cupric Sulphate ($Cu S O_4 (H_2 O)_5$), commonly called blue vitriol, is the commonest salt of copper. When the blue crystals are deprived of their water of crystallization by heat they crumble into a white powder, and this dry salt is an excellent re-agent for the discovery of moisture, as it turns blue when brought in contact with any mixture from which it can absorb water.

When hydric chloride is added to a blue aqueous solution of cupric sulphate the liquid becomes green, owing to the formation of cupric chloride.

When ammonia is added gradually to a solution of cupric sulphate, a basic cupric sulphate is at first precipitated; and this precipitate dissolves readily on the addition of more ammonia, forming a deep blue solution, which may be considered as containing ammonic sulphate combined with ammonic cuprate. The compound can be obtained in crystals, containing $(N H_3)_4 Cu S O_4 H_2 O$.

Ammonic carbonate also precipitates salts of copper, and

when added in excess dissolves the precipitate, forming a dark blue liquid.

Cupric phosphate is precipitated on mixing cupric sulphate with hydro-di-sodic phosphate. The salt appears to contain copper in the place of both sodium and hydrogen of the sodium salt—

$$2\,H\,Na_2\,P\,O_4 + 3\,Cu\,S\,O_4 = Cu_3\,(P\,O_4)_2 + \\ + 2\,Na_2\,S\,O_4 + H_2\,S\,O_4.$$

Arsenious acid forms with cupric oxide a green salt insoluble in water, which can be precipitated by mixing cupric sulphate with an excess of solution of arsenious acid, and then dropping in ammonia until the solution becomes neutral.

173. Cadmium (Cd = 112, = 2 vols.; melting-point, 320°; boiling-point, 860°; sp. gr. 8.6 to 8.7; vapour density = 56) is a comparatively rare metal, which is found associated with zinc, and which presents considerable analogy with zinc.

Cadmium forms a brown oxide (Cd O), and its salts are colourless unless the acid be coloured. They are for the most part crystallizable. Ammonia precipitates white cadmic hydrate, and an excess of ammonia dissolves the precipitate.

Cadmic oxide is not soluble in potash. Potassic cyanide dissolves it readily, but sulphuretted hydrogen precipitates the whole of the metal as sulphide from this solution.

Cadmic sulphide is a beautiful yellow compound. It does not dissolve in ammonic sulphide. With hydric sulphate, chloride, or nitrate, cadmium forms soluble salts.

All the metals of the previous group and of this group are precipitated by zinc from solutions of their salts.

CHAPTER XXVIII.

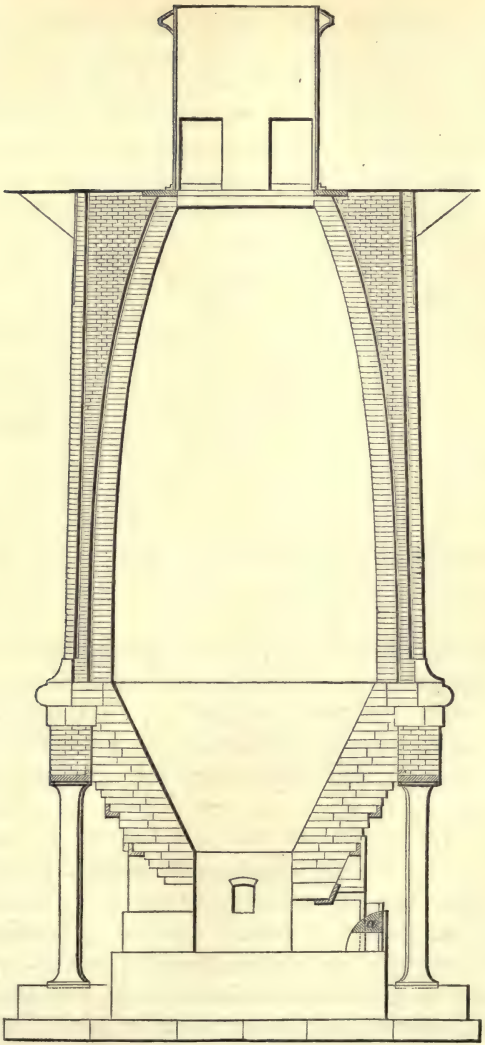
174. Iron (Fe=56; density, 7.84). This most important of metals is rarely found native. Its ores are chiefly of two kinds—viz. oxides and carbonates. Among the former the most important are magnetic iron ore (Fe^3O_4), specular iron ore or red hæmatite (Fe^2O_3), and brown hæmatite $(Fe^2O_3)_2(H_2O)_3$.

Ferrous carbonate sometimes occurs nearly pure, and is then called spathic iron ore. It occurs abundantly mixed with clay and other mineral bodies, and is then called clay-iron stone. The black band is ferrous carbonate containing bituminous matter.

Many ores of iron are deprived of their most volatile constituents by roasting, before they are introduced into the furnace for reduction.

The **Blast Furnace** is a gigantic structure 50 to 80 feet high, supplied at the top alternately with coal or coke, iron ore, and limestone, which gradually sink down until they ultimately run out at the bottom of the furnace, partly as molten cast-iron, partly as liquid calcic and aluminic silicates, &c. called slag. Air is forced in at the bottom of the furnace to support the combustion of the coals, and it is found advantageous to heat this blast of air to at least the melting-point of lead before it enters the furnace. Hot carbonic acid[a] and

[a] Some recent researches seem to shew that at the high temperature of this furnace, the carbon is at once burnt to carbonic oxide without passing through the preliminary stage of carbonic acid.



Vertical Section of Blast Furnace.

steam pass upwards together with the nitrogen of the air, and coming in contact with white-hot carbon the two former gases are reduced to carbonic oxide and hydrogen. As soon as a mass of ore thrown in at the top has descended sufficiently to be heated by the hot mixture of nitrogen, carbonic oxide, and hydrogen, it becomes gradually reduced to spongy metallic iron, mixed with the clay and limestone, &c. which were present in the ore. The gases take up oxygen from the ore and pass over into carbonic acid and steam, but a considerable proportion of them remains unburnt.

The spongy metallic iron, mixed with stones and clay, &c. descends to hotter parts of the furnace, where the iron combines with more carbon, forming liquid ferrous carburet, while the lime unites with the silica and alumina, &c. forming the liquid slag.

The liquid ferrous carburet settles down in the deep hearth at the bottom of the furnace, from which it is let out occasionally by the removal of a plug of clay; while the slag runs off from the top of the hearth, in proportion as it is formed.

While the iron is combining with carbon it also combines with silicon, sulphur, phosphorus, &c., and these substances are present in crude cast-iron (called pig), in various proportions, besides occasional admixtures of manganese, aluminium, and other metals, which are not to be regarded as impurities.

Liquid iron appears to take up a little more than 5 per cent. of carbon, corresponding to the proportion $Fe_4 + C$, and when the molten compound is rapidly cooled a 'white' crystalline mass is obtained of extreme hardness and brittleness.

When the molten carburet is allowed to cool slowly, some of the carbon crystallizes out on its surface in scales like plumbago, while some particles of carbon remain dispersed among the crystals of iron, forming a mass of 'grey' or

'mottled' fracture. The presence of certain foreign bodies —such as manganese, sulphur, or phosphorus—in the carburet prevents this separation of the carbon in slow cooling. Spiegeleisen is a kind of cast-iron containing 5 per cent. or more of manganese, and no carbon crystallizes out from it even on the slowest cooling.

When **White Iron** is heated with hydric chloride it dissolves, with evolution of hydrogen possessing a peculiar odour, and a lesser amount of carbon is found in the liquid when the iron has dissolved. The hydrogen owes its smell to the presence in it of volatile compounds of carbon and hydrogen.

When **Grey Cast-iron** is dissolved in the acid salt, it leaves numerous fragments of carbon, which cannot be driven off by the action of the chloride, and the hydrogen which is evolved contains very little of the volatile compounds of carbon and hydrogen.

In explanation of these different results it has been suggested that the hydrogen which is being evolved from the hydric chloride may be able to change places with iron of the compound $Fe^4 + C$, and thus to pass off in combination with carbon, but cannot combine with carbon which is present in the state of graphite.

White iron melts more easily and rapidly than grey iron, as this latter has gradually to combine with the carbon which is mechanically mixed with it, and to reproduce the fusible carburet.

The specific gravity of cast-iron varies from 7 to 7.25, and is sometimes even higher. Its tensile strength varies from that which will bear a strain of 6 tons on the square inch, up to more than double that strength.

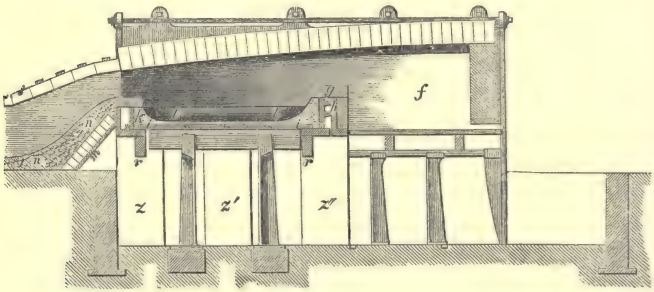
The stiffness of cast-iron is measured by the weight which a straight pillar of it having 1 square inch thickness can support. It varies from 23 tons to upwards of 50 tons.

The lighter varieties of cast-iron are, both as regards tenacity and stiffness, inferior to the denser varieties, and the easiest way of judging of the strength of any specimen of cast-iron is accordingly to take its specific gravity.

Large and massive castings of iron take so long to cool that the particles have time to arrange themselves in large crystals, whereby the strength of the mass is diminished.

Castings of great superficial hardness are obtained by using an iron mould, which 'chills' the particles next to it so rapidly that the carbon remains in great part combined or very intimately mixed with the iron.

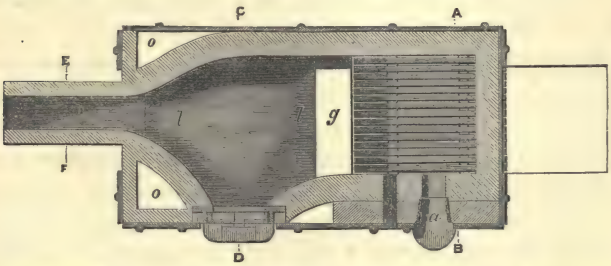
175. In order to make **Malleable Iron** from pig-iron a good quality should be selected and melted in a shallow hearth over which the flames from a reverberatory furnace are playing. Air is allowed to pass into the molten mass and



Vertical Section of Puddling Furnace.—*f* Furnace; *g* fire-bridge; *h* air space in fire-bridge; *i* cast-iron bottom plates; *k* bed of slag; *l* molten iron on the hearth; *m* plate, supporting fire-bricks; *n* slag; *r* cast-iron bearers; *z z′ z″* piers of brickwork.

to oxidize its surface, forming carbonic acid and ferric oxide, and this oxide is stirred about by a workman so as to come in contact with the molten ferrous carburet below. At the end of the process the mass is heated by itself for some time, all air being excluded from the furnace.

Carbon is thus burnt out of the ferrous carburet, partly by the direct action of atmospheric oxygen, partly by the action of the oxygen of ferric oxide, formed on the surface of the mass; and the mass gets thicker and more tenacious in proportion as the carbon is more and more fully removed, until at last it is rolled about on the hearth in the form of a large ball or 'bloom' of soft sticky iron, adhering to the end of the workman's iron rod. This process of decarburizing iron is called 'puddling.'



Horizontal Section of Puddling Furnace.—*a* fire-hole; *g* fire-bridge; *l* hearth containing iron; *o* hollow spaces; A, B, C, E, F plates outside the brickwork; D door for stirring the charge.

These blooms are brought while still hot under a steam hammer or a powerful press, so as to beat or press out the slag and other impurities which they contain, and to unite the particles of iron uniformly together. By repeatedly heating the iron and working it about, its quality is further improved if necessary. In many cases it is customary to subject cast-iron to a process of refining, for the removal of the greater quantity of its impurities previous to puddling. A more rapid process of decarburizing iron has been introduced of late years by Mr. Bessemer, and has been found very advantageous when applied to certain qualities of iron. Bessemer runs the liquid cast-iron into a large pot of refractory clay, and blows air rapidly through it. Intense heat

is evolved, partly by the combustion of the carbon, partly also by combustion of iron; and the fluid mass is kept in violent agitation by the nitrogen and carbonic oxide which are passing through it. In this manner the carbon and silicon are completely removed, and the temperature becomes so high that the metallic iron is left in a fluid state. It is generally run into moulds, in which it is mixed with spiegeleisen in sufficient quantity to yield a metal with about one-half per cent. of carbon.

176. A process has recently been devised for the manufacture of iron, free from phosphorus and sulphur, which will undoubtedly supersede the use of the blast furnace. It consists in melting the ore with suitable fluxes in a regenerative gas furnace, and then running the molten ore into a spherical rotating furnace, raised to a white heat, where it is mixed with some kind of carbonaceous matter, as coke or powdered anthracite. At the end of the reaction the liquid slag is run out through a trap-door brought to the lowest position, while the metal, collected into a ball, is lifted out by proper appliances. The melting furnace is reverberatory, and is connected at the back by two pairs of flues with two pairs of regenerators, in such a way that while the gas and air enter the furnace through one pair, the products of combustion pass out through the other pair, giving up their excess of heat to the mass of brickwork through which they pass. As soon as this pair is sufficiently hot, the direction of the current is reversed by means of valves, the entering gas and air now being heated by the hot pair of regenerators, while the pair which has become cold is again heated by the escaping gases.

The converting furnace consists of a spherical chamber capable of rotation about a horizontal axis, and connected by two pairs of flues with two pairs of regenerators in the manner above described.

Another process of decarburization is that by which so-called **Malleable Cast-iron** is made. It consists in packing the cast-iron utensils into a stoneware vessel, and filling up with hæmatite or smithy scales the spaces which are left. The whole is then kept at a good red heat for several days, or even for a week, and the carbon gradually passes out from the iron in the form of carbonic oxide.

This result is owing to the action of carbonic acid and steam on the carbon of the cast-iron. These gases are reduced by carbon at a red heat—

$$C+CO_2=2CO; \qquad C+H_2O=CO+H^2;$$

and the products formed ($CO+H$) come in contact with the ferric oxide which surrounds the cast-iron, and are oxidized by it into carbonic acid and steam, which again penetrate into the cast-iron, and carry out more of its carbon. It is scarcely practicable to remove by this process the carbon to the depth of more than half an inch from the surface of the casting.

Pure metallic iron is a very soft metal, and is valuable for purposes in which tenacity alone is required. A bar of wrought iron of 1 square inch section ought to carry a dependent weight of 20 tons, and the best specimens of iron carry considerably more.

Iron dissolves readily in dilute acid hydrogen salts, but strong hydric nitrate covers it with a film of anhydrous ferric oxide, which prevents the further action of the nitrate, or even of dilute nitrate. This film is easily removed by the action of reducing agents, and the **passive iron** is thereby rendered active again, and capable of dissolving in dilute nitrate.

177. Metallic iron gradually absorbs oxygen when exposed to air in presence of moisture, forming ferric oxide, commonly called rust; and the presence of a particle of oxide on the surface of iron causes it to undergo oxidation more

rapidly than it otherwise would do. The presence of a particle of copper or tin, or of any one of the metals hitherto described, exerts a similar action in accelerating the process of rusting. Iron does not rust when its surface is moistened with a solution of sodic carbonate, or any other alkaline liquid.

It decomposes steam at a red heat, liberating hydrogen, and forming magnetic oxide of iron. M. Deville has found that the iron continues to be oxidized until the liberated hydrogen reaches a certain proportion, dependent upon the temperature of the iron. If when this point has been attained some hydrogen be withdrawn, a fresh quantity of hydrogen is liberated by the decomposition of an additional amount of water. He has also found that if the proportion of the water vapour be kept constant, the proportion of liberated hydrogen is less, the higher the temperature of the iron. Some of the steam passes over with the hydrogen undecomposed. At a white heat iron even liberates potassium from potassic hydrate.

Iron reduces carbonic acid in a similar manner at a red heat, forming carbonic oxide, which passes over with undecomposed carbonic acid.

Carbonic oxide is also decomposed by metallic iron at a red heat, carbon being taken up by the iron, and carbonic acid being formed. It is probable that in this process ferrous carburet and oxide are simultaneously formed by the absorption of carbonic oxide, and that the ferrous oxide is subsequently reduced by a second molecule of carbonic oxide.

178. Steel is manufactured largely by this process, which is called cementation. Plates of good soft iron are arranged in a stoneware box with alternate layers of charcoal, and the box is closed and heated for several days to a bright red heat. Carbon gradually penetrates into the iron, and the process is usually continued until about 1.5 per cent. of

carbon have been taken up. The oxygen of the air enclosed in the box forms carbonic oxide, and this gas penetrates into the iron. Two molecules of carbonic oxide give up an atom of carbon to the iron, while carbonic acid passes out. The carbonic acid which is formed in the process is reduced again by the surrounding charcoal to carbonic oxide, which carries another atom of carbon into the iron. The steel first obtained in this manner is called 'blistered steel,' from the appearance which it presents; and its composition is far from uniform throughout each plate. It is subjected to various mechanical processes, of which the effect is to mix its various parts more uniformly; but the only process which attains this object completely is fusion, and cast-steel is accordingly the most homogeneous variety of that valuable compound. Steel can be hardened by the process of tempering, and softened again by so-called annealing. The higher the temperature from which steel is suddenly cooled by immersion in oil the greater is its hardness or so-called temper; and by again heating the steel utensil and allowing it to cool slowly it is softened or annealed. Steel is also valuable for its elasticity.

179. Iron forms two basic oxides—ferrous oxide (Fe O) and ferric oxide ($Fe^2 O_3$). It also forms an acid with more oxygen.

Ferrous Oxide is obtained in combination with water by the action of potash or ammonia on a solution of ferrous sulphate. The precipitate is a white hydrate, and it absorbs oxygen with great rapidity, turning first blue and ultimately brown. The hydrate dissolves in ammonic chloride.

Ferric Oxide is found in brilliant crystals called specular iron ore. It is best prepared artificially by precipitating ferric chloride or ferric sulphate by ammonia, and heating the precipitate after due washing. Potash combines with the sesquioxide when used for its precipitation.

There are several hydrates. The precipitate first formed by an excess of ammonia is said to be the normal hydrate $Fe^2 O_6 H_6$, but it speedily loses half its water—

$$2\,Fe^2 H_6 O_6 - 3\,H_2 O = Fe^4 O_9 H_6.$$

There are also oxy-hydrates of the respective composition $Fe^2 O_2 (H O)_2$ and $Fe^2 O (H O)_4$.

Magnetic oxide of iron is considered to be a compound of ferrous oxide with ferric oxide ($Fe^2 O_3 Fe O$).

There are many evidences of the fact that ferrous oxide is a stronger base than ferric oxide. Thus, hydrated ferrous oxide added to a solution of ferric sulphate precipitates the sesquioxide. Baric carbonate precipitates ferric oxide from a solution of the ferric chloride, while carbonic acid is evolved—

$$3\,Ba C O_3 + Fe^2 Cl_6 = 3\,C O_2 + Fe^2 O_3 + 3\,Ba Cl_2.$$

The precipitated oxide contains water in combination.

The baryta salt has no action upon ferrous chloride under similar circumstances.

180. Ferrous Cyanide is chiefly known in combination with other cyanides. There are, however, two important blue compounds, which consist of iron and cyanogen.

One of these is called **Prussian blue**, and gave rise to the name prussic acid. It is formed by mixing a solution of potassic ferrocyanide ($Fe Cy_6 K_4$) with a solution of a ferric salt, and potassic ferrocyanide constitutes an excellent reagent for iron when present in the form of a ferric salt. With a solution of ferric chloride the reaction occurs thus, $3\,Fe Cy_6 K_4 + 2\,Fe^2 Cl_6 = Fe^7 Cy_{18} + 12\,K Cl$; dilute acid hydrogen salts have no action on Prussian blue, but it is readily decomposed by alkalies. Thus, potash reproduces potassic ferrocyanide from it, and precipitates ferric oxide—

$$Fe^7 Cy_{18} + 12\,K H O = 3\,Fe Cy_6 K_4 + 2\,Fe^2 O_3 + 6\,H_2 O.$$

The other blue compound is usually called Turnbull's blue.

It is precipitated by mixing a solution of potassic ferricyanide with a ferrous salt—

$$Fe^2\,Cy_{12}\,K_6 + 3\,Fe\,Cl_2 = Fe^5\,Cy_{12} + 6\,K\,Cl.$$

With potash it reacts thus—

$$Fe^5\,Cy_{12} + 8\,K\,H\,O = 2\,Fe\,Cy_6\,K_4 + Fe^2\,H_6\,O_6 + Fe\,H_2\,O_2.$$

Ferrous cyanide can be obtained in combination with prussic acid, forming a white crystalline compound called hydric ferrocyanide ($Fe\,Cy_6\,H_4$). This salt is precipitated from a solution of potassic ferrocyanide by the addition of hydric chloride and ether. It speedily absorbs oxygen from the air and turns blue.

Ferrous Carbonate ($C\,O_3\,Fe$) is precipitated by the action of an alkaline carbonate on ferrous sulphate. It is a white powder which rapidly absorbs oxygen from the air, giving off its carbonic acid and becoming ferric oxide. The salt dissolves in water containing free carbonic acid, and is present in this form in the water from some springs, from which ferric oxide is deposited by the evaporation of carbonic acid into the air and combination with oxygen.

Ferrous Chloride ($Fe\,Cl_2$) is obtained in solution by dissolving the metal in hydric chloride. Like most of the ferrous salts this compound has a pale green colour. When exposed to the air it gradually turns yellow by absorption of oxygen, and deposits a ferric oxy-chloride. Ferrous chloride can be obtained as a white salt by evaporating its solution to dryness and heating the residue.

Ferric Chloride ($Fe^2\,Cl_6$) can be obtained by burning iron wire in an excess of dry chlorine. It is deposited in the form of shining scales, which can easily be volatilized by heat. M. Deville took the vapour density of this body by ascertaining the weight which filled a globe surrounded by the vapour of boiling sulphur, and he found it to correspond to the formula $Fe^2\,Cl_6 = 2$ vols. Once dissolved in water the salt cannot be recovered by evaporation, as its solution

decomposes very readily, into hydric chloride which goes away, and ferric oxide which remains behind. A solution of this or of any other ferric salt, provided the acid contained in the salt be not possessed of reducing properties, withstands boiling without undergoing any reduction to ferrous salt.

Iodine seems only to form at ordinary temperatures one compound with iron, a ferrous iodide, for when a solution of ferric chloride is mixed with potassic iodide, iodine is set free; $Fe^2Cl_6 + 6KI = 2FeI_2 + I^2 + 6KCl$.

There are two well-known definite sulphides of iron—a black ferrous sulphide (Fe S) and a yellow disulphide (FeS_2), commonly called pyrites. Iron burns with considerable intensity in the vapour of sulphur, forming the ferrous sulphide. This compound is readily fusible and dissolves in dilute sulphate or chloride with evolution of sulphuretted hydrogen—

$$FeS + 2HCl = FeCl_2 + H^2S.$$

Sulphuretted hydrogen gas does not decompose the ferrous salts, but on the addition of ammonia a black precipitate, consisting of ferrous sulphide combined with water, is formed. This precipitate dissolves very easily in acid salts, and rapidly absorbs oxygen from the air, the iron becoming ferric oxide, while the sulphur remains for the most part unoxidized.

Ferric salts are reduced by sulphuretted hydrogen with deposition of sulphur, thus—

$$Fe^2Cl_6 + H_2S = 2FeCl_2 + 2HCl + S.$$

Pyrites is of considerable value as a source of sulphur, for the preparation of sulphuric acid. It is sometimes decomposed by a process of distillation, by which less than half the sulphur is expelled from the pyrites. It is more common to roast the pyrites so as to oxidize both its constituents, leading the sulphurous acid into the lead chamber. Ferric di-sulphide is not dissolved by hydric chloride nor by the sulphate.

181. Ferrous Sulphate ($Fe\,S\,O_4$), commonly called green vitriol or copperas, is formed when iron is dissolved by dilute hydric sulphate. It is prepared on a large scale by the action of air upon moist pyrites.

Common green vitriol contains seven molecules of water of crystallization ($S\,O_4\,Fe\,(H_2\,O)_7$), which can be driven off by heat. Stronger heat decomposes the dry sulphate, sulphurous acid coming off and ferric di-oxy-sulphate being formed—

$$2\,Fe\,S\,O_4 = S\,O_2 + Fe^2\,O_2\,S\,O_4.$$

On further heating, this oxy-salt is in its turn decomposed, sulphuric acid coming off and red ferric oxide remaining behind.

Ferrous sulphate can also be obtained in combination with four or three or two molecules of water of crystallization. The crystals of the ordinary salt absorb oxygen from the air and turn brown, being transformed into the ferric oxy-disulphate $Fe^2\,O\,(S\,O_4)_2$.

Ferrous sulphate combines with potassic sulphate, forming the double salt $Fe\,K_2\,(S\,O_4)_2\,(H_2\,O)_6$. Similar double salts are formed with other alkalies.

Normal **Ferric Sulphate** ($Fe^2\,(S\,O_4)_3$) can be obtained by dividing a convenient quantity of oil of vitriol into three equal portions, saturating two of these portions, after dilution, with metallic iron, then adding the third portion to this solution and evaporating down to dryness with an excess of hydric nitrate. The salt is nearly white. It gives off its sulphuric acid on heating.

Ferric sulphate combines with ammonic sulphate, forming a salt which crystallizes in beautiful violet-coloured octohedrons; $(S\,O_4)_4\,Fe^2\,(N\,H_4)_2\,(H_2\,O)_{24}$.

Ferrous phosphate ($(P\,O_4)_2\,Fe_3$) can be obtained as a white powder by double decomposition; it is found in combination with water as a mineral called vivianite.

Ferric Phosphate ($Fe^2P_2O_8(H_2O)_4$) is precipitated as a brownish-white gelatinous salt on mixing a ferric salt with a neutral and soluble phosphate. The salt is dissolved by acid salts but is not dissolved by the acetate, and its solution in hydric chloride is precipitated by the addition of ammonic acetate, the chloride being neutralized by the ammonia, and acetate liberated in its stead.

CHAPTER XXIX.

182. Aluminium (Al=27.5; density 2.56 to 2.67) is prepared by the action of metallic sodium on the double chloride of aluminium and sodium.

It is a bluish-white metal, remarkable for its great lightness. A bar of aluminium, when suspended by a string, rings with a clear and musical note when gently tapped. The metal can be drawn into fine wire or rolled into plates. The surface becomes dull when the metal is long exposed to the air. Hydric nitrate in a dilute state has scarcely any action on aluminium, but the chloride dissolves it rapidly with evolution of hydrogen, forming aluminic chloride ($Al^2 Cl_6$). Dilute hydric sulphate dissolves it with difficulty.

Aluminium can be melted in an open crucible without oxidation, and cast into moulds. It forms with copper a very beautiful alloy of great strength and elasticity, and of the colour of gold. This aluminium bronze contains 90 per cent. of copper and 10 of aluminium.

183. There is only one oxide of aluminium, the so-called **Alumina**, which occurs crystallized as corundum. The close analogy of alumina with ferric oxide has decided chemists to class it among the sesquioxides, and to give the formula $Al^2 O_3$.

It is best obtained in a state of purity from commercial sodic-aluminate. The solution of this compound is acidulated by hydric chloride, evaporated to dryness and heated with frequent stirring. On washing the mass with water, pure

alumina is left behind. Alumina can be precipitated as a hydrate by ammonia, or ammonic carbonate from a solution of one of its salts, but from its gelatinous consistency it is a troublesome precipitate to wash. As long as it retains water in combination it can be easily dissolved by caustic potash or by acid salts, but it is insoluble in hydric chloride after having been exposed to a red heat. Potassic hydrate, however, combines with it at a red heat, and renders it again soluble in acid salts. Alumina is not reduced by carbon or hydrogen, even at the highest temperatures.

It combines with many colouring matters, forming solid compounds, by the aid of which the colours are fixed upon cotton or linen. When exerting this action alumina is termed a **mordant.** A very common material for mordanting consists of aluminic sulphate (either pure or combined with ammonic sulphate), in which two-thirds of the sulphuric acid are replaced by acetic acid. This double salt, consisting of alumina combined partly with acetic acid, partly with sulphuric acid, very readily allows its acetic acid to escape by evaporation, while aluminic hydro-sulphate is left behind. A piece of calico moistened with a solution of the salt and hung up in warm and moist air becomes impregnated with aluminic hydro-sulphate by the process called 'ageing,' which is nothing else than an evaporation of acetic acid.

If subsequently immersed in a solution of madder dye, the cloth becomes dyed, by a combination of the mordant contained in it with the colouring matter.

184. Aluminic Chloride ($Al^2 Cl_6$) cannot be formed by driving of the water from a solution of the salt, as it decomposes during that operation into hydric chloride and alumina. Finely-divided alumina is prepared from sodic aluminate, and intimately mixed with coal-dust. The mixture is heated to bright redness in a fire-clay tube, through which chlorine is passing. Carbonic oxide escapes while

aluminic chloride sublimes up to the colder parts of the tube; $Al^2O_3 + 3C + 3Cl^2 = Al^2Cl_6 + 3CO$.

The vapour of aluminic chloride is 134 times as heavy as hydrogen, as can be seen from the fact that Al^2Cl_6 occupies two volumes.

Aluminium does not combine with sulphur in the wet way. Ammonic sulphide added to a solution of a salt of alumina precipitates the white aluminic hydrate, while sulphuretted hydrogen is liberated—

$$Al^2Cl_6 + ((NH_4)_2S)_3 + 6H_2O = Al^2O_6H_6 + \\ + 3H_2S + 6NH_4Cl.$$

185. Aluminic Sulphate is prepared by heating clay with hydric sulphate, and precipitating, as Prussian blue, the iron which dissolves with it. The salt crystallizes with water; $Al^2(SO_4)_3(H_2O)_{18}$.

Its solution is intensely acid. The double salt containing aluminic sulphate, combined with potassic sulphate, has long been known by the name of alum. It occurs in regular octohedral crystals, containing 24 molecules of water—

$$Al^2K_2(SO_4)_4(H_2O)_{24}.$$

Of late years it has been to a great extent superseded in this country by ammonia alum—

$$Al^2(NH_4)_2(SO_4)_4(H_2O)_{24}.$$

Sodium and silver form double sulphates similar to them, and having the same crystalline form.

These alums cannot be separated by crystallization; and a crystal of one of them grows regularly in a solution of another alum, just as well as in a solution of salt of the same kind; the particle of one alum arranging themselves symmetrically with those of another.

Ferric sulphate, chromic sulphate, and manganic sulphate form double salts with the sulphates of the alkalies, perfectly similar in constitution and in crystalline form to the alums, and capable of crystallizing with them in the same crystals.

Compounds of analogous chemical constitution and of nearly identical crystalline forms are called **Isomorphous.**

Aluminic phosphate ($P_2 O_8 Al^2$) is precipitated in the form of a white gelatinous mass by the decomposition of alum by hydro-di-sodic phosphate. It dissolves in acid salts, except in hydric acetate, or in potash, and so closely resembles alumina that some care is required for the detection of the phosphate in it. Ammonic nitro-molybdate affords the most rapid means of discovering hydric phosphate when combined with alumina.

186. Silica occurs very commonly in combination with alumina and other bases in minerals, and the various kinds of **clay** are products of the gradual decomposition of felspar and similar double silicates by the action of carbonic acid, water, and ammonia. Common **felspar** is represented by the formula $(Si O_2)_6 Al^2 O_3 K_2 O$. In some varieties the potash is more or less completely replaced by soda, while ferric oxide is generally present in small quantity, taking the place of some of the alumina. The alkali is gradually dissolved out from these minerals by aqueous and atmospheric action, while the minerals crumble down to a soft mass, and most kinds of clay still retain some of the alkali of the original rock in combination.

One of the most important properties of clay is that of absorbing water and forming with it a soft pasty compound, through which the rootlets of plants can work their way, and from which they can take up water containing potash, ammonia, phosphoric acid, &c. in solution, for their vital functions. Clay combines in a similar loose manner with ammonia, and holds it, like the water, in readiness for the plants. Some clays are so tenacious as to retain too much wet on the surface of the soil, and to prevent its draining down to the subsoil. These are very justly termed 'cold,' for much of the heat from the sun's rays which fall on such

a wet soil is absorbed in evaporating the water, and lost to the plants whose growth is dependent upon it. Many such clays are greatly improved by burning, a process which not only diminishes their tenacity but also renders the alkali remaining in them more soluble.

The most refractory clays, such as Stourbridge clay (which is used for the manufacture of fire-bricks), are not only those most free from alkalies, but also those containing the largest proportion of silica. The formula $(Si\,O_2)_6\,Al^2\,O_3$ represents the composition of such a clay. Many clays have a composition approaching more nearly to the formula $(Si\,O_2)_3\,Al^2\,O_3$.

Earthenware, pottery, and bricks are made of plastic clay, the latter having a considerable proportion of sand mixed up with the clay before it is moulded into shape.

Stoneware and china are made of superior qualities of clay, and glazed by the addition of felspar, in sufficient quantity to form at the high temperature of the kiln a glass which fills up the pores of the clay.

187. Chromium (Cr = 52.5). This metal has been reduced from its oxide by charcoal at a very high temperature, and by potassium from its chloride. It has, however, been but little studied as yet.

The mineral from which chromium compounds are usually prepared is the chrome iron-stone ($Cr_2\,Fe\,O_4$).

Chromium forms three distinct oxides, and probably a fourth. Two of its oxides are bases—viz. chromous oxide ($Cr\,O$) and chromic oxide ($Cr^2\,O_3$). The third is an acid ($Cr\,O^3$), chromic acid.

Chromous oxide is analogous in its salts to ferrous oxide, but these salts absorb oxygen far more rapidly and retain it more forcibly than the corresponding salts of iron.

Chromic Oxide is a bright green powder, much valued as a paint. It is obtained by heating its hydrate, precipitated

by excess of ammonia from a solution of chromic chloride. Chromic oxide forms under special conditions green salts, which are uncrystallizable. It also forms another class of salts, distinguishable from the above by their violet colour and by the power of crystallizing.

Chromic hydrate dissolves in potash, and is precipitated from that solution by boiling.

In order to separate it from alumina the two oxides should be dissolved in cold potash in excess, and the chromic oxide oxidized into chromic acid by the action of chlorine. After acidulation of the liquid by hydric chloride the alumina can be precipitated alone by ammonic carbonate.

Chromic oxide behaves like alumina to ammonic sulphide; for the precipitate produced by that re-agent in the solution of a chromic salt is chromic hydrate, while sulphuretted hydrogen is liberated—

$$Cr^2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Cr^2H_6O_6 + \\ + 3(NH_4)_2SO_4 + 3H_2S.$$

188. Chromic Acid (CrO^3) can be obtained in the form of crimson needles by leading the vapour of chromic fluoride ($CrFl_6$) into a moist platinum crucible.

It is a dibasic acid, and forms a neutral potash salt (CrO_4K_2), isomorphous with neutral potassic sulphate. Potassic chromate is yellow, and its colouring power is so great as to afford a delicate test for the presence of the salt in a solution.

Potassic dichromate, commonly called red chromate, is the salt most commonly manufactured. Its composition is represented by the formula $Cr^2O_7K_2$.

Chromic acid is reduced by boiling with strong aqueous hydric chloride, a green colour taking the place of the original red one. Chlorine is given off, and chromic chloride is left in solution—

$$2CrO^3 + 12HCl = Cr^2Cl_6 + 6Cl + 6H_2O.$$

A similar reduction with precipitation of sulphur is effected by sulphuretted hydrogen, in liquids containing chromic acid mixed with an acid salt—

$$2\,Cr\,O^3 + 6\,H\,Cl + 3\,H_2\,S = Cr^2\,Cl_6 + 3\,S + 6\,H_2\,O.$$

When a salt of chromic acid is heated with oil of vitriol and sodic chloride, a red vapour consisting of chlorochromic acid is given off. The reaction is thus represented—

$$Cr\,O_4\,K_2 + 2\,Na\,Cl + 2\,H_2\,S\,O_4 = Cr\,O_2\,Cl_2 + \\ + S\,O_4\,K_2 + S\,O_4\,Na_2 + 2\,H_2\,O.$$

An excess of oil of vitriol is needed in the reaction in order to combine with the water which is formed.

When chromic acid is heated with strong hydric sulphate it gives off half its oxygen, forming chromic sulphate—

$$2\,Cr\,O^3 + 3\,H_2\,S\,O_4 = Cr^2\,(S\,O_4)_3 + 3\,O + 3\,H_2\,O.$$

This mixture affords one of the most powerful means of oxidizing carbon at comparatively low temperatures.

Chromic acid forms a yellow neutral salt with baryta which is insoluble in water but soluble in hydric chloride, also a red baric dichromate ($Cr^2\,O_7\,Ba$), which dissolves in water.

The neutral argentic chromate is a crimson salt insoluble in water but soluble in hydric nitrate.

Neutral plumbic chromate ($Cr\,O_4\,Pb$) is a yellow insoluble salt much used as a yellow paint.

There is also a basic plumbic chromate of an orange colour.

189. Two chlorides of chromium are known—viz. the chromous chloride $Cr\,Cl_2$, a white powder obtained by heating chromic chloride in a stream of hydrogen, and the chromic chloride $Cr^2\,Cl_6$, a pink salt which becomes green on combining with water.

Chlorochromic Acid ($Cr\,O_2\,Cl_2$), mentioned above, is one of the most important compounds theoretically. Its molecule occupies two volumes in the state of vapour—

$$Cr\,O_2\,Cl_2 = 2\text{ vols.},$$

and is accordingly 77·75 times as heavy as that of hydrogen. The red vapour condenses to a heavy oily liquid, having a boiling-point at 118°. Chlorochromic acid is dissolved by water with decomposition ($Cr O_2 Cl_2 + H_2O = Cr O^3 + 2 H Cl$), and cannot be recovered by evaporation.

Chromic fluoride is easily formed by distilling red potassic chromate with ammonic fluoride and an excess of strong hydric sulphate in a platinum retort—

$$K_2 Cr^2 O_7 + 12 N H_4 F + 7 H_2 S O_4 = 2 Cr F_6 + \\ + K_2 S O_4 + 6 (N H_4)_2 S O_4 + 7 H_2 O.$$

190. Uranium (Ur = 120). The chief ore of uranium is pitch-blende. The metal forms a protoxide analogous to chromous oxide, which does not give up its oxygen at a red heat to hydrogen. It also forms a yellow uranic oxide ($Ur^2 O_3$), which is soluble in ammonic carbonate, hydric chloride, nitrate and sulphate. The sesquioxide forms an insoluble phosphate. Uranium is used for preparing a beautiful yellow glass with a tinge of green, and which is remarkable for its fluorescence.

CHAPTER XXX.

191. Cobalt (Co = 58.5) is found associated with nickel, arsenic, and some other metals.

It can be reduced from its oxides by charcoal at a high temperature, and can with difficulty be melted to a compact button of a specific gravity of 8.95. Cobalt is slightly magnetic.

It forms a cobaltous oxide Co O, which is a brown powder, when obtained by heating a higher oxide in a stream of carbonic acid. The compounds which cobaltous oxide forms by reacting on acids are generally blue when free from water, and not unfrequently of the same colour in presence of water mixed with a strong acid salt. In combination with water they are generally red. Ammonic sulphide added to one of them forms a black precipitate of cobaltous sulphide, which is scarcely soluble in hydric chloride. Potash precipitates a pink cobaltous hydrate—

$$Co O_2 H_2,$$

which rapidly absorbs oxygen from the air and acquires a dingy green colour.

Ammonia forms a similar precipitate, but an excess of the reagent dissolves it, and the solution gradually becomes brown in contact with air, by absorbing oxygen. If ammonic chloride be present in sufficient quantity potash does not precipitate the solution.

Baric carbonate does not decompose a solution of cobaltous chloride in the cold, but if chlorine be passed through

the mixture a cobaltic chloride is formed which is entirely decomposed by the baric salt—

$$Co^2 Cl_6 + 3\,Ba\,C\,O_3 = Co^2 O_3 + 3\,C\,O_2 + 3\,Ba\,Cl_2.$$

A mixture of cobaltic oxide and strong hydric chloride gives off chlorine when heated and forms a solution of cobaltous chloride.

A concentrated solution of potassic nitrite added to a solution of a salt of cobalt acidulated with hydric acetate, gives a yellow precipitate of a double nitrite of potassium and cobalt. This affords a convenient means of distinguishing cobalt from nickel, as the latter metal does not yield a similar compound.

Potassic cyanide precipitates cobaltous salts, forming cobaltous cyanide, but this precipitate dissolves readily in an excess of potassic cyanide, and the double cyanide thus obtained decomposes prussic acid at the boiling-point, evolving hydrogen and forming a double salt of great stability, and having the empyrical formula $Co^2 Cy_{12} K_6$, which is explained as being made up of cobaltic cyanide ($Co^2 Cy_6$) combined with 6 K Cy. Cobalt can easily be detected by the bright blue colour which its oxide imparts at a high temperature to glass, to borax, or any other salts of the alkalies, or to alumina. With zinc oxide it forms a green compound which is used as a paint, and with magnesia a pale pink compound.

Smalt is the powder of a blue glass coloured by cobalt, and Thénard's blue is a compound of cobaltous oxide with phosphoric acid and alumina.

Cobaltic oxide is a black powder which dissolves in hydric sulphate with evolution of oxygen, in hydric chloride with evolution of chlorine, and is very slightly acted upon by hydric nitrate.

Cobaltous Chloride can be obtained in the form of blue scaly crystals when dry. It is deposited from aqueous solu-

tion, in combination with six molecules of water, in ruby-red crystals. The red solution becomes blue on the addition of a strong acid salt, but recovers its red colour on dilution.

Cobaltous sulphate ($S O_4 Co (H_2 O)_7$) is an easily crystallizable salt, which combines with potassic sulphate, forming the salt $(S O_4)_2 Co K_2 (H_2 O)_6$.

192. Manganese ($Mn = 55$; sp. gr. 8). The most important ore of this metal is the peroxide $Mn O_2$, which is usually called 'manganese' in commerce.

The metal is reduced from its oxide by charcoal at a high temperature, and melts with difficulty into a button. Hydrogen does not reduce the metal from its chloride, whereas the chlorides of iron, cobalt, and nickel are reduced by hydrogen to the metallic state.

Manganese remains bright when kept in dry air, but in presence of moisture it gradually crumbles down to a brown oxide. The only alloy of the metal of commercial value is spiegeleisen, which consists essentially of iron, with 5 to 15 per cent. of manganese, and 5 per cent. of carbon.

Manganese forms five definite oxides, two of which—the manganous oxide and manganic oxide—are bases, and are known in the free state as well as in compounds.

The two highest oxides are manganic acid ($Mn O^3$) and permanganic acid ($Mn^2 O_7$). These are only known in combination with bases in the manganates (such as $K_2 Mn O_4$), and permanganates (such as $K_2 Mn^2 O_8$).

Manganous oxide can be obtained by heating the carbonate in an atmosphere containing no free oxygen. It is analogous to ferrous oxide in its salts, and its salts are of a faint pink colour in presence of water.

Manganous hydrate ($Mn O_2 H_2$) is precipitated by potash from a solution of a manganous salt. It dissolves readily in ammonic chloride, and in this solution gradually absorbs oxygen, and goes down as manganic hydrate.

A process has recently come into use, called Weldon's process, from the name of the inventor, for the recovery of manganese from the acid liquor left in the manufacture of chlorine from 'manganese' and hydric chloride. The white manganous hydrate is precipitated by means of an excess of milk of lime, and then air is blown into the alkaline liquid, the result being to convert from 80 to 85 per cent. of the manganous hydrate into the peroxide.

Manganic Oxide (Mn^2O_3) is found in crystals, and is termed 'braunite' by mineralogists. It is analogous to ferric oxide in its salts, but a solution of any of its salts is reduced by boiling to the corresponding manganous salt; thus manganic sulphate ($Mn^2(SO_4)_3$) is reduced to manganous sulphate ($MnSO_4$).

Manganic Peroxide is a black compound, insoluble in hydric nitrate, soluble in strong hydric chloride at a high temperature, with evolution of chlorine and formation of manganous chloride; $MnO_2 + 4HCl = MnCl_2 \quad Cl^2 + 2H_2O$. It is also soluble in strong hydric sulphate at a high temperature, with evolution of oxygen.

It can be prepared by heating manganous carbonate with constant stirring in contact with the air, as long as its colour continues to become darker. The black powder thus formed is a compound of manganic peroxide and manganous oxide, and the latter oxide can be dissolved out from it by hydric nitrate.

Manganic peroxide gives off one-third of its oxygen at a strong red heat, leaving a brown powder (Mn^3O_4), which corresponds in composition to the magnetic oxide of iron—

$$3MnO_2 = Mn^3O_4 + O^2.$$

193. Manganous Carbonate is found crystallized in the same form as ferrous carbonate. It is precipitated as a white powder by the action of sodic carbonate on man-

ganous chloride, but it always loses a little carbonic acid, and acquires a brownish colour during the operation of drying.

Manganous Chloride ($Mn Cl_2$) is formed in large quantities in the preparation of chlorine, by dissolving manganic peroxide in hydric chloride.

It can be obtained nearly pure by evaporating these 'chlorine residues' to dryness, and heating the mixture to a dull red heat. On dissolving afterwards in water the iron is left undissolved in the form of ferric oxide, and the crystals which are obtained from the filtered solution consist of manganous chloride, containing a trace of cobalt. This impurity can be removed by stirring up with the solution a little freshly-precipitated manganous sulphide, and filtering off from the black cobaltous sulphide—

$$Mn S + Co Cl_2 = Mn Cl_2 + Co S.$$

The manganous chloride is deposited from solution in combination with four molecules of water of crystallization—

$$Mn Cl_2 (H_2 O)_4.$$

Baric carbonate has no action in the cold on a solution of manganous chloride, but if chlorine be passed into the mixture the manganese is precipitated as manganic oxide or peroxide, by a process analogous to that which occurs in the corresponding treatment of cobaltous chloride.

Manganic chloride ($Mn^2 Cl_6$) is no doubt formed by the action of chlorine in the cold on a solution of the manganous chloride, as well as by dissolving manganic oxide in cold hydric chloride; but the salt gives off one-third of its chlorine with such extreme readiness that it has never been obtained in the dry state.

Manganous Sulphide ($Mn S$) is precipitated in combination with water by the action of ammonic sulphide on a solution of a manganous salt. The sulphide is flesh-coloured. It dissolves with the utmost facility in acid salts and even in

hydric acetate, and can easily be separated from cobaltous sulphide by dilute hydric chloride.

Manganous Sulphate ($Mn S O_4$) crystallizes usually with five molecules of water, but at lower temperatures it forms crystals with seven molecules of water. The salt combines with potassic sulphate, forming a double salt which corresponds in its constitution to the potassio-ferrous sulphate.

Manganic sulphate is also known in combination with potassic sulphate. The salt crystallizes in regular octohedral crystals, having the composition—

$$Mn^2 K_2 (S O_4)_4 (H_2 O)_{24}.$$

This salt is isomorphous with alum, and is called manganese alum.

194. Potassic Manganate ($Mn O_4 K_2$) is a deep green salt, which is readily formed by heating any salt of manganese with an excess of potassic hydrate in contact with the air. The minutest trace of manganese can be discovered by the green colour which is formed by this process. The salt has been crystallized, and found to be isomorphous with potassic sulphate and with potassic chromate.

A solution of potassic manganate decomposes very rapidly when exposed to the air; the addition of a little acid accelerates the change, and causes the green solution to turn purple. This change of colour obtained for the salt the name mineral chameleon. The change of colour is due to the formation of potassic permanganate ($K_2 Mn^2 O_8$), and is accompanied by potash and manganic peroxide (hydrated). It may be thus represented by an equation—

$$3 K_2 Mn O_4 + 2 H_2 O = K_2 Mn^2 O_8 + Mn O_2 + 4 K H O.$$

Potassic Permanganate ($Mn^2 O_8 K_2$) is a salt of a deep purple colour, so intense that very small quantities of manganese can be detected in the wet way by its formation. A mixture of plumbic peroxide and hydric nitrate, heated with a salt of manganese, gives rise to the formation of a small

quantity of permanganate. The salt is usually prepared by decomposing potassic manganate by a little hydric nitrate, and crystallizing the solution. The crystals of potassic permanganate are isomorphous with those of the perchlorate.

A solution of potassic permanganate oxidizes organic bodies with extreme facility, and is accordingly used as a disinfecting material.

195. Nickel (Ni = 58.5) is remarkable for its great analogy to cobalt. It is chiefly made for the sake of an alloy called German silver, which contains copper, zinc, and nickel in various proportions, generally approaching to two parts of copper, one of zinc, and one of nickel.

Nickel forms a nickelous oxide (Ni O), of which the salts are green in presence of water and yellow when dry.

There is also a nickelic oxide ($Ni^2 O_3$), of which no salts are known.

Nickelous Chloride is a beautiful green salt, which crystallizes with nine molecules of water.

Its solution in water is not decomposed in the cold by baric carbonate, either by itself or in presence of chlorine; and it can accordingly be purified from cobalt by the action of these reagents.

Potash gives a green precipitate of nickelous hydrate. Ammonia gives a similar precipitate, but when added in excess dissolves the precipitate, forming a blue solution. This solution of nickel in ammonia is precipitated by the addition of an excess of potash.

Potassic cyanide precipitates nickel cyanide, and when added in excess dissolves the precipitate. Mercuric oxide precipitates all the nickel from this solution as oxide, but has no action on the solution of the potassio-cobaltic cyanide $Co^2 Cy_{12} K_6$.

Black nickel sulphide is precipitated by ammonic sulphide, and dissolves in hydric chloride. It also dissolves to some

extent in an excess of ammonic sulphide, forming a dark brown solution.

Nickel Sulphate is a green salt, which crystallizes readily from water with the composition $S O_4 Ni (H_2 O)_7$. These crystals have the same form as those of ferrous sulphate and cobaltous sulphate. Nickel sulphate combines with potassic sulphate, forming the salt $(S O_4)_2 Ni K_2 (H_2 O)_6$.

196. Zinc ($Zn = 65$; melting-point 433°C; boils at a red heat; density 7.1 to 7.3). This metal occurs sometimes in combination with sulphur, in an ore called 'blende.' Another ore of zinc is 'calamine,' which is a zinc carbonate. The ore is first roasted, and the crude zinc oxide obtained in this manner is mixed with coal, and distilled at a bright red heat. Cadmium frequently accompanies zinc. It then comes over in the beginning of the distillation, and is recognized by the brown 'smoke' (cadmic oxide) formed by the combustion of its vapour. The vapour of zinc burns with a bluish-white flame, depositing white zinc oxide.

Zinc is a very crystalline metal. At a temperature somewhat below 150° it is very soft and ductile, but at about 200° it is exceedingly brittle, and can be powdered in a mortar.

Zinc becomes tarnished in moist air by absorbing oxygen. It decomposes steam and carbonic acid at a red heat. In dilute hydric sulphate or chloride it dissolves, giving off hydrogen, and forming zinc sulphate ($Zn S O_4$), or zinc chloride ($Zn Cl_2$). Its action upon hydric nitrate depends upon the strength of the acid salt and the temperature at which the action takes place. Nitric oxide, nitrous oxide, nitrogen, or ammonia are formed, according to circumstances. Zinc dissolves in hot caustic potash, giving off hydrogen. It precipitates from acid liquids all the metals of the two first groups. It reduces the ferric salts to ferrous salts.

Zinc is much used in the alloy with copper, called **brass.**

The proportions of the two metals in brass are subject to considerable variation, the zinc amounting sometimes to no more than 30 per cent. of its weight, sometimes to nearly 50 per cent. The presence of 1 to 1.1 per cent. of iron improves greatly the quality of brass. An alloy of this kind, called sterro-metal, combines, after hammering, an extraordinary degree of tenacity and of elasticity.

197. Zinc combines in one proportion only with oxygen, and the **oxide** shews great analogy with magnesia in its salts, and with a variety of other oxides known to consist of one atom of metal combined with one atom of oxygen. These analogies decide in favour of the formula Zn O. Zinc oxide is most economically prepared by burning the vapour of the metal as it issues from the neck of the reduction apparatus. It can also be obtained by heating zinc carbonate, or hydrate, or by roasting the sulphide. When obtained by any of these last-named processes it has a yellowish tinge, which does not belong to zinc oxide made by combustion of the metal.

Zinc Carbonate ($ZnCO_3$) cannot be obtained by the action of an alkaline carbonate on a solution of a salt of zinc, as carbonic acid escapes and an oxy-salt is precipitated. The normal carbonate occurs, however, in nature crystallized.

Zinc Chloride ($ZnCl_2$) is obtained by dissolving the metal in hydric chloride, evaporating to dryness, and fusing the residue. During these operations the mass continues liquid, passing from the state of concentrated aqueous solution to that of molten salt. At a red heat the salt evaporates. It is exceedingly soluble in water, and its solution is sold as a disinfecting fluid.

Zinc Sulphide (Zn S) is precipitated as a white gelatinous mass by the action of sulphuretted hydrogen on a solution of zinc sulphate, or of the chloride or nitrate. The precipitation is, however, prevented by the presence of a

sufficient quantity of hydric sulphate or other hydrogen salt of a mineral acid, and accordingly is arrested as soon as sulphuretted hydrogen has liberated this proportion of acid from one of the zinc salts.

Zinc acetate is completely decomposed by sulphuretted hydrogen, even though a large quantity of hydric acetate be present in the solution; and this reaction affords the most convenient means of separating zinc from nickel, as the latter metal is not, or very slightly, precipitated from such a mixture. Zinc sulphide is also precipitated by the action of sulphuretted hydrogen on a solution of zinc oxide in potash.

Zinc Sulphate, or white vitriol ($Zn S O_4$), can be obtained by gently roasting blende. At a high temperature the sulphate is decomposed, giving off its sulphuric acid, partly as such, partly in the form of a mixture of sulphurous acid and oxygen. The common crystals of the salt are of the composition $S O_4 Zn (H_2 O)_7$. There are also compounds containing a lesser number of molecules of water of crystallization. There is a double salt with potassic sulphate—

$$(S O_4)_2 Zn K_2 (H_2 O)_6.$$

A solution of zinc sulphate dissolves a considerable quantity of metallic zinc, giving off hydrogen and forming basic salts.

198. Thallium (Tl = 203; melting-point, 283°; density, 11.9) has been found most abundantly in the deposit which occurs in the flues, when certain kinds of pyrites are burnt in the manufacture of oil of vitriol. It was discovered by the brilliant green line which its vapour gives in the spectrum. In its physical properties the metal has considerable resemblance to lead, but its specific heat and the characters of its salts leave no room for doubt that it is monovalent in its ordinary salts and trivalent in some others.

Thallium is precipitable from a solution of its sulphate. Ammonic sulphide precipitates dark brown thallious sulphide

from solutions of its salts. Thallium becomes tarnished when exposed to the air, and has a decidedly alkaline taste like potash when placed upon the tongue. Its oxide ($Tl_2 O$) is soluble in water, and absorbs carbonic acid from the air. Thallious chloride ($Tl Cl$) and iodide ($Tl I$) are but slightly soluble in water. There is also a thallic chloride ($Tl Cl_3$). Platinic chloride unites with thallious chloride, forming the double salt $Pt Cl_6 Tl_2$, which is considerably less soluble in water than the corresponding platinum salt of cœsium. Thallious sulphate ($Tl_2 S O_4$) unites with aluminic sulphate, forming the salt $(S O_4)_4 Al^2 Tl_2 (H_2 O)_{24}$, which is a true alum. The salts of thallium are exceedingly poisonous. Thallium is easily detected by the green colour which its compounds give to the flame.

The oxides of the rare metals **Cerium, Lanthanum, Didymium, Yttrium,** and **Glucinum** are to be classed with those of the last-described metals.

Glucina ($G O$) is contained in the emerald, and has much resemblance to alumina. It dissolves, however, in a solution of ammonic chloride on boiling, and can thus be separated from alumina. It also dissolves in ammonic carbonate. Yttrium, Lanthanum, and Didymium appear to form only protoxides analogous to the cerous oxide ($Ce O$); but cerium also forms a ceric oxide ($Ce^2 O_3$). The four protoxides form sulphates which combine with potassic sulphate, forming double salts, such as $(S O_4)_2 Ce K_2$, which are nearly insoluble in a saturated solution of potassic sulphate.

CHAPTER XXXI.

199. Barium (Ba = 137; sp. gr. about 4). This metal is but little known in the free state. It has been obtained by decomposing fused baric chloride by a galvanic current, or, in combination with mercury, by decomposing a solution of that salt in water containing free hydric chloride, while the negative pole was in contact with a drop of mercury. Sodium or potassium are not able to decompose baric chloride in an open crucible.

Baryta (Ba O) is a strong base. There is also a higher oxide called baric peroxide, which is neutral. Baryta occurs frequently in combination with sulphuric acid in the mineral called Heavyspar. Its carbonate, called Witherite, is also found in considerable quantities.

Baryta is most easily prepared by heating baric nitrate to redness in an earthen crucible. The outer portions of the mass contain silica from the crucible. It is a grey porous mass. Water combines with baryta very energetically, and the hydrate ($Ba\ O_2\ H_2$) thus formed may be heated to a bright red heat without losing its water. The best way to obtain the hydrate is to heat a mixture of baric carbonate and coal to a bright red heat for two or three hours, to dissolve in water after cooling, and allow the carbon and residual carbonate to settle.

The solution of baryta is intensely alkaline to test-paper. It deposits on evaporation crystals of the composition $Ba\ O_2H_2\ (H_2\ O)_8$. These crystals dissolve in about

twenty times their weight of cold water, and in a much smaller quantity of boiling water. The solution is usually called baryta water. It absorbs carbonic acid from the air, depositing baric carbonate. It precipitates from solutions of their salts all the basic oxides of the preceding groups. It also expels ammonia from its salts.

Baric Peroxide ($Ba O^2$) is formed either by heating baryta or its hydrate in oxygen or air. It gives up its second atom of oxygen at a bright red heat. To obtain it in a state of purity, its solution in dilute hydric chloride should be precipitated by baryta water, and the precipitate deprived of its water by gentle heat.

Baric Nitrate ($Ba(NO_3)_2$) may be prepared by dissolving finely-powdered baric carbonate in dilute hydric nitrate; but a better process is to add the nitrate to a solution of baric sulphide—

$$Ba S + 2 H N O_3 = (N O_3)_2 Ba + H_2 S.$$

The salt crystallizes without any water of crystallization, but it generally decrepitates when heated, owing to water enclosed mechanically by some of the crystals, bursting them asunder by its evaporation.

Baric nitrate can be precipitated in great part from a saturated solution by the addition of strong hydric nitrate.

200. Baric Carbonate can be precipitated by an alkaline carbonate from baric nitrate. The salt is almost perfectly insoluble in water, but an appreciable quantity of it is dissolved by free carbonic acid. Baric carbonate parts with its carbonic acid at an intense white heat.

Baric oxalate is insoluble in water but soluble in hydric nitrate or chloride, and to a very slight extent even in hydric acetate.

Baric cyanide ($(C N)_2 Ba$) dissolves in water with an alkaline reaction. It is decomposed by carbonic acid.

Baric Chloride ($Ba Cl_2$) is one of the most commonly

used salts of baryta. It is made by dissolving either the carbonate or sulphide in hydric chloride. On a large scale it has been prepared by adding manganese residues (impure manganous chloride) to a solution of baric sulphide, and filtering off the metallic sulphides which are precipitated.

It crystallizes from water in plates which contain two molecules of water ($Cl_2 Ba (H_2 O)_2$). It is far more soluble in water than the nitrate, and its saturated solution is precipitated by strong hydric chloride. It is insoluble in alcohol if no water be present.

A solution of the salt can be evaporated to dryness and the residue heated without decomposing the salt.

Baric chlorate ($(Cl O_3)_2 Ba$) crystallizes from water in beautiful crystals, which are used in the manufacture of green fire.

Iodine decomposes baryta water rapidly, forming a white precipitate of baric iodate, while baric iodide remains in the solution—

$$6 Ba H_2 O_2 + 6 I^2 = Ba (I O_3)_2 + 5 Ba I_2 + 6 H_2 O.$$

Baric fluoride ($F_2 Ba$) is insoluble in water but soluble in hydric chloride.

Baric Sulphide (Ba S) is obtained by heating for several hours an intimate mixture of finely-ground coal and baric sulphate—

$$S O_4 Ba + 2C^2 = S Ba + 4 C O.$$

The sulphide dissolves readily in hot water; but the solution, if concentrated, deposits on cooling crystals of baric hydrate, whilst sulph-hydrate remains dissolved and turns yellow by absorption of oxygen—

$$2 Ba S + 2 H_2 O = Ba O_2 H_2 + Ba S_2 H_2;$$
$$Ba S_2 H_2 + O = Ba S_2 + H_2 O.$$

Cupric oxide decomposes a solution of baric sulphide, taking up its sulphur, and leaving baric hydrate in solution.

Baric sulphide is a strong sulphur base. Its solution dissolves sulphur, forming a baric pentasulphide S_5Ba.

Baric hyposulphite (S_2O_3Ba) is very slightly soluble in water.

Baric sulphite is a white precipitate, insoluble in water but soluble in hydric nitrate or chloride.

Baric Hyposulphate (S_2O_6Ba) is most easily prepared by dissolving manganic peroxide in an aqueous solution of sulphurous acid, and precipitating the solution by baric sulphide. The sulphite and sulphate present in the liquid go down as baryta salts, together with the manganous sulphide. The filtered liquid is evaporated and deposits crystals of baric hyposulphate.

Baric Sulphate (SO_4Ba) is one of the commonest minerals containing this valuable base.

It is perfectly insoluble in water, and its particles are formed so instantaneously when any soluble sulphate comes in contact with a solution containing a salt of barium, that they have no time to arrange themselves into crystals, but go down in the form of an impalpable powder. The salt is not soluble in hydric chloride, even on boiling. It dissolves to an exceedingly slight extent in hydric nitrate, and, moreover, is liable to carry baric nitrate down with it, when formed in a solution containing a nitrate. In this case the baric sulphate is found to impart an alkaline reaction to water after it has been heated to redness. Baric sulphate dissolves to a slight extent in strong hydric sulphate, and is precipitated from that solution by the addition of water. It is not decomposed by heat.

Baric seleniate is very much like the sulphate, but can be distinguished from it by the fact that it dissolves in boiling hydric chloride with evolution of chlorine and formation of selenious acid.

Hydric phosphate forms with baryta a normal salt—

$$(PO_4)_2Ba_3,$$

which is insoluble in water, but which dissolves in hydric nitrate or chloride. It also dissolves in hydric phosphate, forming a phosphate of hydrogen and baryta $(P O_4)_2 Ba H_4$, tetra-hydro-baric phosphate.

Hydric phosphite forms an insolu' le baryta salt containing

$$(P O_3)_2 Ba_2 H_2 (H_2 O)_n.$$

This salt dissolves in hydric phosphite, forming the salt

$$(P O_3)_2 Ba H_4.$$

There is also a soluble and crystallizable hypophosphate $(P O_2)_2 Ba H_4$, which is easily obtained by boiling phosphorus in baryta water and crystallizing the solution, after filtering it off from the phosphate and phosphite which are formed at the same time.

Silicic fluoride combines with baric fluoride, forming a compound represented by the formula $Si F_6 Ba$.

Hydric fluo-silicate precipitates the barium almost completely from the nitrate or chloride, leaving in solution hydric nitrate or chloride. The baric fluo-silicate decomposes when heated to redness, giving off silicic fluoride and leaving baric fluoride.

Boracic acid forms a compound with baryta which is nearly insoluble in water, but which dissolves in various neutral salts; so that boracic acid cannot be carried down completely from a solution in combination with baryta.

Hydric arseniate behaves very like the phosphate towards baryta. The arsenite also forms a neutral salt insoluble in water.

Chromic acid forms a neutral baric salt ($Cr O_4 Ba$) of a bright-yellow colour, insoluble in water and in hydric acetate but soluble in hydric chloride. It also forms an acid salt, which is deposited from aqueous solution in red crystals.

201. Strontium (Sr = 87.5; sp. gr. 2.58). This metal exhibits in its compounds a close analogy with barium.

It occurs as sulphate (called cœlestine), carbonate, and other salts.

Strontic hydrate is less soluble in water than baric hydrate. The nitrate and chloride are, however, more soluble than the corresponding baryta salts.

Strontic nitrate is manufactured for the preparation of red fire. Strontic chloride is somewhat soluble in alcohol, and can thus be separated from baric chloride.

Strontic sulphate is to a very slight extent soluble in water, and a solution of it precipitates salts of baryta.

Hydric fluo-silicate does not precipitate a moderately concentrated solution of a salt of strontia. Potassic chromate does not precipitate a dilute solution of a salt of strontia nor a concentrated solution containing hydric acetate.

202. Calcium (Ca=40; sp. gr. 1.56) is reduced in the same manner as barium, and has a reddish tinge approaching to that of copper.

Lime (Ca O) is one of the commonest and most important of bases. It is most commonly made by heating calcic carbonate. When lime is wanted for laboratory use, black marble is the best material for this operation, as the organic matter contained in it reduces the carbonic acid, and thus aids its expulsion. Some varieties of chalk or limestone contain a good deal of silica, which unites with the lime during the operation of burning, and diminishes greatly the value of the product for most purposes.

Lime is infusible, but by long exposure to an intense heat it becomes hard from semi-fusion. It is far less soluble in water than strontia, for it requires 600 or 800 times its weight of cold water for its solution. When such 'lime water' is heated, a deposit of lime makes its appearance, for boiling water dissolves only about half as much lime as cold water.

Dry lime (commonly called quicklime) combines with a

molecule of water with evolution of great heat, and crumbles into a light powder having the composition $Ca\,O_2\,H_2$. The operation is commonly called 'slaking.'

Calcic hydrate—unlike baric hydrate—loses its water at a dull red heat.

Water containing calcic hydrate in suspension is usually termed milk of lime.

203. Calcic nitrate ($(N\,O_3)_2Ca$) is an exceedingly soluble salt, which can with difficulty be obtained in crystals containing $(N\,O_3)_2Ca\,(H_2\,O)_4$. Even in the dry state calcic nitrate dissolves in alcohol.

Calcic Carbonate ($Ca\,C\,O_3$) occurs as calc-spar, and in many other minerals. A variety of calc-spar is found in Iceland in transparent and colourless masses, which are valuable for the construction of polarizing instruments. Calcic carbonate is occasionally found in crystals belonging to a different system from that to which calc-spar belongs. This mineral is called arragonite.

Calcic carbonate is precipitated by an alkaline carbonate from a solution of calcic chloride or nitrate. The precipitate is gelatinous when first formed, and its particles subsequently arrange themselves more closely together in small crystals, enclosing at the same time some of the liquid from which they are formed.

Calcic carbonate dissolves very slightly in water, but quite sufficiently to diminish the value of the water for many purposes by making it 'hard.'

The presence of free carbonic acid increases greatly the solubility of calcic carbonate, owing to the formation of a hydrocalcic carbonate $(C\,O_3)_2\,Ca\,H_2$.

The water from many springs contains this double salt, and, on exposure to the air, deposits calcic carbonate, while half of the carbonic acid evaporates.

Calcic carbonate dissolves on boiling in ammonic chloride,

the ammonic carbonate being carried off by the steam as fast as it is formed—

$$CO_3Ca + 2NH_4Cl = Cl_2Ca + CO_3(NH_4)_2.$$

If the products of this reaction be collected and mixed in cold aqueous solution, they decompose one another, and reproduce calcic carbonate and ammonic chloride. Hydric oxalate forms with lime a very insoluble salt, which is usually resorted to for the complete precipitation of lime. The oxalate is nearly insoluble in hydric acetate, but it dissolves in nitrate or in chloride. The salt is easily decomposed by heat, its acid breaking up into carbonic oxide, which escapes, and carbonic acid, which remains at first in great part with the lime, but is in its turn expelled by stronger heat.

Calcic Chloride (Cl_2Ca) is a waste product formed in several manufactures, and is of value for drying gases, as well as for the artificial production of cold. It undergoes a partial decomposition during the process of driving off water from the moist salt; but the dry mass, although basic, does not absorb carbonic acid. Calcic chloride crystallizes from a very concentrated aqueous solution, in combination with six molecules of water, of which four are easily expelled by gentle heat. These crystals are used for freezing mixtures. The dry chloride evolves heat on combining with water. Calcic chloride dissolves readily in alcohol.

Chloride of Lime, or bleaching-powder, are names given to a mixture containing calcic hypochlorite, and valuable only in proportion to the quantity of this salt which it contains. It is prepared by passing chlorine over trays in which slaked lime is spread out. When chloride of lime is exposed to the air, the calcic hypochlorite contained in the substance is decomposed by carbonic acid, with liberation of hypochlorous acid, which is gradually given off. The salt is decomposed by heat into calcic chloride and chlorate—

$$3\,CaCl_2O_2 = (ClO_3)_2Ca + 2\,CaCl_2.$$

Calcic fluoride, or **fluorspar** (F_2Ca), is found in beautiful cubical crystals, sometimes green, sometimes purple, while other specimens are amber-coloured. It is very slightly soluble in water, but dissolves in hydric chloride.

Calcic sulphide (S Ca) can be obtained by the action of sulphuretted hydrogen on red-hot lime. It is very slightly soluble in water, but is gradually decomposed by water, especially with the aid of heat, into calcic hydrate and calcic sulph-hydrate, the latter compound dissolving while the former remains in great part undissolved—

$$2\,Ca\,S + 2\,H_2O = Ca\,O_2\,H_2 + Ca\,S_2\,H_2.$$

Milk of lime dissolves large quantities of flowers of sulphur when the two substances are boiled together. The yellow solution thus obtained consists of a mixture of calcic penta-sulphide and calcic hyposulphite—

$$3\,Ca\,O_2\,H_2 + 6\,S^2 = 2\,Ca\,S_5 + Ca\,S_2\,O_3 + 3\,H_2O.$$

At a red heat calcic sulphate is formed, and a lower calcic sulphide.

Calcic sulphite ($S\,O_3\,Ca$) is a salt insoluble in water. It dissolves, however, in sulphurous acid, with formation no doubt of a hydro-calcic sulphite.

204. Calcic Sulphate is found crystallized without water, and is then called 'anhydrite.' It occurs more commonly in combination with two molecules of water—

$$S\,O_4\,Ca\,(H_2O)_2,$$

and is then called 'gypsum,' or plaster of Paris. This compound loses its water of crystallization at about 130°, and the powder of the salt, dried at this temperature, solidifies to a coherent mass by resuming its water of crystallization, when mixed with a suitable quantity of water. If it has been exposed to a temperature of nearly 200°, it solidifies much more slowly when moistened. The salt requires about 400 parts of water for its solution, and is accordingly precipitated by the action of a soluble sulphate

upon calcic chloride, if less than this proportion of water be present. A saturated aqueous solution of calcic sulphate forms an immediate precipitate when mixed with a solution of a salt of baryta, and it forms more slowly a smaller precipitate when mixed with a soluble salt of strontia.

Calcic sulphate is insoluble in alcohol and in water containing a large quantity of alcohol.

Calcic Phosphate is the chief constituent of bone-ash. It can be obtained by precipitation, but has then generally some hydrogen in place of a part of its calcium. Its formula is $(P O_4)_2 Ca_3$. The salt dissolves in hydric nitrate or chloride. It is decomposed by hydric sulphate, with formation of calcic sulphate and the soluble tetra-hydro-calcic phosphate $(P O_4)_2 Ca H_4$.

A mixture obtained in this manner is largely manufactured as a manure, and goes by the name of superphosphate of lime. Hydric acetate dissolves calcic phosphate easily if the salt be first dissolved in the chloride and precipitated as a gelatinous mass by ammonia.

Calcic silicate occurs in crystals having the composition $Si O_3 Ca$. The mineral is called tabular spar.

Calcic silicate is probably the compound which is formed when hydraulic mortar becomes hard. A mixture of clay and lime is ground up very finely together for the preparation of this material, and the action of water upon it induces the combination of lime with silica and alumina to which the hardening is due.

Building mortar is a fine mixture of slaked lime with sand, and its hardening is attributed to the gradual absorption of carbonic acid by the lime. A calcic silicate is, however, doubtless formed on the surface of the granules of sand.

An artificial stone of great strength is manufactured by precipitating calcic chloride gradually by a solution of sodic

silicate, in presence of a large quantity of sand. Calcic silicate is at first formed in a gelatinous state, and gradually contracts on drying, and binds the granules of sand together very firmly.

205. Magnesium ($Mg = 24$). This metal is analogous to the alkaline earths in some of its properties, but is more closely connected with zinc and cadmium. It is prepared by the action of sodium on magnesic chloride, and is purified by distillation. It is a white metal, and does not tarnish in dry air. It can be pressed into wire, and a piece of its wire when kindled in a flame burns with considerable brilliancy, forming a white powder, magnesia ($Mg O$).

Magnesia is widely diffused through the mineral kingdom. The sea-water owes its bitter taste to the presence of a salt of magnesia; and magnesic sulphate is found occasionally in mineral waters. The earth itself is usually made by calcining magnesic carbonate. It is nearly insoluble in water, but when put upon faintly-reddened moist litmus-paper, it imparts a blue colour to the paper. Magnesic hydrate is precipitated as a gelatinous mass by potash, and even by ammonia, from the sulphate or nitrate, &c. It is also precipitated by baryta. Magnesia dissolves readily in ammoniacal salts, and for this reason ammonia gives no precipitate in the solution of a salt of magnesia, containing originally much acid salt, or salt of ammonia.

Magnesia becomes pink when moistened with a solution of cobaltous nitrate and heated before the blow-pipe.

Magnesic nitrate ($(N O_3)_2 Mg$) is an exceedingly soluble salt which deliquesces in moist air. It crystallizes from a concentrated solution with six molecules of water, and is soluble in alcohol.

Magnesic Carbonate occurs frequently with calcic carbonate in one crystal. It can be precipitated in combination with water from a magnesia salt by double decomposition,

but is very liable to lose some of its carbonic acid, taking up water instead. The salt is easily deprived of its carbonic acid by calcination. It dissolves in ammonic carbonate, forming a double carbonate, which crystallizes out from the solution on standing. Magnesic carbonate dissolves in carbonic acid water to a far greater extent than calcic carbonate, and a solution of magnesic hydro-carbonate is used in medicine under the name of 'fluid magnesia.' The solution has an alkaline reaction. The solution is readily decomposed by boiling, and even by exposure to the air, carbonic acid going off.

Magnesic oxalate ($C^2\,O_4\,Mg$) is very slightly soluble in water but readily soluble in ammonia salts, and lime can accordingly be separated completely from magnesia by means of an oxalate in such a solution.

Magnesic chloride ($Cl_2\,Mg$) cannot be obtained in a pure state by evaporation of its aqueous solution, for hydric chloride passes off with the water and a basic salt is left. It is now prepared for the manufacture of magnesium by evaporating the very concentrated solution in a stream of gaseous hydric chloride. The chloride melts readily. It is exceedingly soluble in water.

Magnesic hydrate is dissolved in considerable quantity by water through which a stream of sulphuretted hydrogen is passed, and forms the magnesic sulph-hydrate $Mg\,S_2\,H_2$.

Magnesic Sulphate ($S\,O_4\,Mg$), commonly called Epsom salts, occurs usually in crystals containing seven molecules of water of crystallization, which are isomorphous with the corresponding crystals of zinc sulphate. One of these molecules of water is supposed to be replaced by potassic sulphate in the double salt $(S\,O_4)_2\,Mg\,K_2\,(H_2\,O)_6$.

Magnesic sulphate dissolves in about three times its weight of cold water, and the solution has the bitter taste which belongs to all soluble salts of the earth. It is not soluble in

alcohol. A bright red heat decomposes magnesic sulphate completely.

One of the most important magnesian salts is an **ammonio-magnesic phosphate,** which has a composition represented by the formula $P O_4 Mg N H_4 (H_2 O)_6$. This salt is very slightly soluble in water, and insoluble in water containing free ammonia. It is, however, deposited very slowly from a dilute solution in which its constituents are brought together. It dissolves readily in acid salts. At a red heat it loses all its water and ammonia, leaving so-called magnesic pyro-phosphate, properly called di-magnesic di-phosphate—

$$2 P O_4 Mg N H_4 (H_2 O)_6 = Mg_2 P_2 O_7 + 2 N H_3 + 13 H_2 O.$$

CHAPTER XXXII.

206. Potassium ($K = 39$; sp. gr. 0.86; melting-point, 62.5°). This remarkable body was first obtained by Davy by the action of a strong galvanic current on potassic hydrate moistened by a small quantity of water. It was afterwards prepared by the action of finely-divided metallic iron on potassic hydrate at a white heat, but is now usually obtained by heating potassic carbonate with charcoal to a white heat.

It is rapidly oxidized by the air even at low temperatures, and must therefore be collected and kept out of contact with the air. At the ordinary temperature potassium is a soft metal of a consistency somewhat similar to soft wax. At a red heat it can be distilled. It decomposes water with great violence, and evolves at the same time sufficient heat to kindle the hydrogen which is given off.

In air or oxygen it burns with formation of a white smoke, which consists of potassic tetroxide (K_2O^4).

When heated in an atmosphere of carbonic acid it decomposes the gas with a bright glowing light, and a deposit of carbon is left in the place which was occupied by the potassium. It absorbs carbonic oxide, forming a detonating compound; and when potassium is reduced by the action of charcoal, a considerable proportion of the product is lost by combining with the carbonic oxide simultaneously formed.

Potassium forms a very strong base called potash, con-

sisting of two atoms of the metal united with one atom of oxygen (K_2O). The anhydrous potash is obtained by heating potassic hydrate with metallic potassium—

$$HKO + K = K_2O + H.$$

207. Potassic Hydrate, or 'caustic potash,' as it is usually called, is commonly prepared by boiling a solution of potassic carbonate with milk of lime. The potassic carbonate is dissolved in about twelve times its weight of water, and heated to the boiling-point in an iron pan. Quicklime (about two-thirds of the weight of the carbonate) is slaked in four times its weight of hot water, and this lime-milk added little by little to the boiling solution of potassic carbonate. A precipitate of calcic carbonate is formed, which should be allowed to settle while the pot is kept carefully covered—

$$K_2CO_3 + CaH_2O_2 = 2\,KHO + CaCO_3.$$

The clear liquid should be siphoned off and evaporated in a metallic vessel without contact with the air.

The residue can be fused, and cast into sticks or any other convenient form. The fusion should take place in a silver vessel.

Potassic hydrate made in this way generally contains a good many impurities — viz. potassic carbonate, sulphate, phosphate, and chloride—besides silica and alumina. Most of these are left behind (as potassium salts) when the potash is dissolved in alcohol. The impurities of the product are mostly due to the impure nature of the materials employed, but neither lime nor potassic carbonate are easily to be obtained in the pure state, and processes have accordingly been devised for preparing potash from materials which are easily obtained pure. One such process is the precipitation of a solution of potassic sulphate by baryta water—

$$SO_4K_2 + BaO_2H_2 = SO_4Ba + 2\,KHO.$$

Another is to fuse potassic nitrate in a copper crucible until no further evolution of gas takes place, and then to continue the heating in presence of some finely-divided metallic copper. The copper reduces nitrogen from a small quantity of nitrite, which cannot easily be decomposed by heat alone.

Potash dissolves animal membranes rapidly, and has thus acquired the title of 'caustic.' It also attacks glass, more especially the softer kinds of glass, and when kept in solution in a glass bottle, it is accordingly liable to contain silica.

It liberates baryta, lime, or magnesia, from solutions of their salts, and expels ammonia readily.

208. Potassic Nitrate, or saltpetre (NO_3K), is formed by the decomposition of nitrogenized animal matter, in contact with clay or other minerals capable of yielding potash, and can be obtained in considerable quantities by washing the earth excavated from the neighbourhood of houses which have been long inhabited, and evaporating the filtered solution till it crystallizes on cooling. It is not unfrequently prepared from sodic nitrate, by crystallizing a mixture of that salt with potassic chloride, the potassic nitrate being less soluble than the sodic salt—

$$NO_3Na + ClK = NO_3K + ClNa.$$

It is usually contaminated with common salt, from which it can be purified by crystallization.

Nitre is chiefly used for the manufacture of gunpowder —a mechanical mixture of charcoal, sulphur, and nitre. The proportions of these materials usually approach that represented by the formula $2\,KNO_3 + S + 3\,C$; and the combustion of the carbon forming $3\,CO_2$, leaves sulphur to combine with the potassium (K_2S) while nitrogen is liberated. Some secondary products always accompany these.

Potassic nitrite (KNO_2) is prepared by cautiously heating the nitrate and purifying the product by crystallization.

Potassic Nitride is obtained by heating potassium in a stream of ammonia gas. The first reaction consists in potassium displacing one atom of hydrogen in the ammonia—

$$NH_3 + K = NH_2K + H;$$

but when this potassic amide is heated, it decomposes into ammonia and potassic nitride—

$$3\,NH_2K = NK_3 + 2\,NH_3.$$

Both compounds are immediately decomposed by water into ammonia and potassic hydrate.

209. Potassic Carbonate (CO_3K_2) is the salt which was originally called potash, from the circumstance of its being contained in the ashes left on the combustion of wood. It is most commonly made by dissolving the ashes of land plants in a small quantity of water, insufficient for the solution of the other constituents of the ash, and evaporating the solution to dryness. A subsequent calcination serves to destroy the organic matter which frequently accompanies the crude potash.

It usually contains sulphates, phosphates, and chlorides, besides silica. For laboratory use, a much purer carbonate can be obtained by fusing hydro-potassic tartrate in a platinum crucible, and dissolving out the carbonate which is formed, from the charcoal which accompanies it.

Potassic carbonate is alkaline to test-paper. It absorbs water readily, and if left long enough in contact with moist air forms a thick oily liquid. It is not soluble in alcohol.

Hydro-potassic Carbonate (CO_3KH) crystallizes out from a solution of potassic carbonate which is placed in contact with carbonic acid. The salt is decomposed by ebullition of its aqueous solution.

Potassic oxalate ($C^2 O_4 K_2$) is a neutral salt obtained by neutralizing sorrel salt by potassic carbonate.

Hydro-potassic oxalate ($C^2 O_4 K H$) is found in the juice of sorrel, and imparts to that plant its acid taste. When hydric oxalate is added to a concentrated solution of this salt, a compound of it with the oxalate is precipitated, having a composition represented by this formula—

$$(C^2 O_4 K H)\ (C^2 O_4 H_2)\ (H_2 O)_2.$$

210. Potassic Cyanide (C N K) can be obtained by fusing potassic ferrocyanide in a closed crucible at a bright red heat, and allowing the iron and carbon to settle to the bottom of the liquid mass. When cold, the crucible must be broken, and the black portion of its contents separated from the white potassic cyanide. The salt is frequently prepared, together with some potassic cyanate, by fusing dry potassic ferrocyanide with about one-third its weight of potassic carbonate. The first reaction is no doubt the formation of ferrous carbonate, but this is speedily reduced to the metallic state, forming potassic cyanate—

$$(Cy)_6 Fe K_4 + C O_3 K_2 = 5 K (Cy) + (Cy) K O + Fe + C O_2.$$

The salt can be purified by crystallization from spirits of wine, and is then obtained in cubes.

Potassic cyanide is formed by heating potassic carbonate with nitrogenized animal matter. It is also found in the gases which rise from the hottest part of the blast furnace.

Its aqueous solution is intensely alkaline, and even carbonic acid decomposes it, liberating prussic acid. At high temperatures potassic cyanide is a powerful reducing agent, taking up an atom of oxygen from ferrous oxide or lead oxide, and forming potassic cyanate (C N K O). This salt can be obtained by fusing potassic cyanide with about three and a half times its weight of litharge, and dissolving the product in hot spirits of wine, which deposits potassic cyanate on cooling. Potassic cyanate is decomposed by

moist air, ammonia escaping, and hydro-potassic carbonate remaining behind; $C O K N + 2 H_2 O = C O_3 H K + N H_3$.

Potassic cyanide also combines readily with sulphur, either while dissolved in water or when fused with sulphur, forming potassic sulphocyanate (C N K S); which is a salt exceedingly soluble in water, and not decomposed by contact with it like the cyanate.

211. Potassic Chloride (Cl K) is prepared from the mother liquor of sea-water, and a considerable quantity of it has been found near Magdeburg mixed with other salts.

It crystallizes in cubes, containing no water of crystallization. At high temperatures the salt is readily volatilized.

Its double salt with platinic chloride ($Pt Cl_6 K_2$) is very slightly soluble in water and insoluble in alcohol. When a sulphate is present in a mixture containing potash, platinic chloride forms a precipitate containing both sulphate and chloride.

Potassic Chlorate ($K Cl O_3$) is a salt largely manufactured for the preparation of lucifer matches. It can be obtained by heating the mixture of potassic chloride and hypochlorite, which is formed by the action of chlorine on caustic potash. The hypochlorite breaks up into potassic chloride and potassic chlorate—

$$3 K Cl O = 2 K Cl + Cl O_3 K.$$

It is usually prepared by adding potassic chloride to a mixture of calcic chloride and calcic chlorate, and evaporating to crystallization—

$$(Cl O_3)_2 Ca + 2 K Cl = 2 K Cl O_2 + Cl_2 Ca.$$

It crystallizes in anhydrous plates.

On decomposing the salt by heat, a portion of it takes up oxygen, and becomes converted into potassic perchlorate ($Cl O_4 K$), which requires a higher temperature for its decomposition. Potassic perchlorate is one of the least soluble of

potash salts in water, and its solubility is still less in presence of alcohol.

Bromine decomposes potash rapidly, forming at once a mixture of potassic bromide and potassic bromate—

$$3\,Br^2 + 6\,K\,H\,O = 5\,K\,Br + K\,Br\,O_3 + 3\,H_2\,O.$$

Iodine acts in a similar manner; and if strong potash be used potassic iodate is speedily deposited. In the manufacture of **Potassic Iodide** it is customary to evaporate to dryness a mixture of the two salts, and to decompose the potassic iodate by heat.

Potassic iodide crystallizes in anhydrous cubes, which are very apt to become tinged by free iodine, if exposed to air containing any acid salt; for hydric iodide, which is at first liberated from them, is rapidly oxidized by the air. The commercial salt sometimes contains a little potassic iodate.

Potassic fluoride ($F^2\,K_2$) is a very soluble salt which crystallizes in cubes. Its solution attacks glass.

Hydro-potassic fluoride ($F^2\,K\,H$) is obtained by crystallizing a mixture of hydric fluoride and potassic fluoride.

Potassic fluo-boride ($B\,F_4\,K$) is a soluble salt which crystallizes from water. It gives off boric fluoride at a red heat, leaving potassic fluoride.

Potassic fluo-silicate ($Si\,F_6\,K_2$) is precipitated by the action of hydric fluo-silicate on a salt of potash, such as nitrate chloride, &c. It is an opalescent semi-transparent precipitate not quite insoluble in water.

212. Potassic Sulphide ($S\,K_2$) is formed by the action of hydrogen or carbon upon potassic sulphate at a red heat. An aqueous solution of it is obtained by dividing a solution of potash into two equal parts, saturating one of them by sulphuretted hydrogen, boiling to expel the excess of sulphuretted hydrogen, and then mixing with the remaining half of the potash. The solution is colourless and strongly

alkaline. Acid hydrogen salts decompose it with evolution of sulphuretted hydrogen, and without any deposition of sulphur. The solution readily dissolves sulphur to the extent of four additional atoms, forming potassic pentasulphide (S^5K_2). Even one atom of sulphur added to the sulphide gives it a yellow colour, and causes a deposition of sulphur when an acid salt is added to the solution—

$$S^2K_2 + 2HCl = SH_2 + 2KCl + S.$$

Carbonic acid decomposes potassic sulphide, hence its 'hepatic' smell.

Potassic Sulph-hydrate (SKH) is obtained by saturating potash by sulphuretted hydrogen, and boiling away the excess of the gas. It crystallizes in colourless crystals. Its solution, as well as that of potassic sulphide, absorbs oxygen from the air, forming potassic hyposulphite.

Potassic sulphite (SO_3K_2) is obtained by decomposing potassic carbonate by sulphurous acid.

Hydro-potassic sulphite (SO_3KH) is formed by the action of the last-named salt on sulphurous acid in presence of water. It is precipitated from its solution by alcohol.

213. Potassic Sulphate (SO_4K_2) is deposited from water in hard crystals, which contain mechanically-enclosed water, but no water of crystallization, and usually decrepitate when heated. The salt is not decomposed by heat. It dissolves in about ten times its weight of cold water, but the addition of hydric chloride increases its solubility by forming potassic chloride and hydro-potassic sulphate, which is more soluble than potassic sulphate itself—

$$SO_4K_2 + HCl = SO_4KH + ClK.$$

Potassic Di-sulphate ($S_2O_7K_2$) crystallizes out from a solution of potassic sulphate in two molecules of hydric sulphate. It gives off sulphuric acid when strongly heated.

Hydro-potassic Sulphate (SO_4KH) is obtained in the preparation of nitric acid in the laboratory. The salt

dissolves in about half its weight of boiling water, but when the solution is crystallized, some crystals of neutral potassic sulphate are deposited among those of the double salt, and by successive crystallizations the whole salt may be decomposed into acid hydrogen salt and neutral salt.

214. The normal **Potassic Phosphate** ($P O_4 K_3$) is obtained by fusing hydric phosphate with an excess of potassic carbonate. It has an alkaline reaction to test-paper. The hydro-di-potassic phosphate ($P O_4 K_2 H$) is a nearly neutral salt; it has not, however, been obtained in crystals. The di-hydro-potassic phosphate ($P O_4 K H_2$) is acid to test-paper.

Arsenic acid forms three salts similar to these.

Antimonic acid forms a soluble compound with two atoms of potassium, and probably one of hydrogen also, which is obtained by fusing the acid with potassic hydrate; and also a salt of the composition $Sb O_4 K H_2 (H_2 O)_2$.

Chromic acid forms two crystallizable salts with potash, viz. the neutral potassic chromate ($Cr O_4 K_2$), which is obtained in yellow crystals isomorphous with potassic sulphate) and potassic dichromate ($Cr_2 O_7 K_2$), the common commercial salt, frequently called, from its colour, red chromate. It is made by fusing chrome-iron-ore with nitre. The crystals are anhydrous.

Potassic Permanganate ($Mn^2 O_8 K_2$) is obtained by decomposing potassic manganate by water, pouring off from the precipitate of manganic peroxide, and evaporating to crystallization. It is obtained in purple needles, isomorphous with potassic perchlorate, and capable of crystallizing with that salt in all proportions.

CHAPTER XXXIII.

215. Sodium (Na = 23; sp. gr. 0.97; melting-point, 98°). This metal is reduced by the action of charcoal at a white heat on sodic carbonate. It distils over in the carbonic oxide which is simultaneously formed, but, unlike potassium, it does not combine with any of that gas. The preparation of sodium is much easier than that of potassium, and the metal is now manufactured in considerable quantities for the reduction of aluminium and magnesium.

Sodium decomposes water, when thrown upon its surface, with less intensity than potassium does, and the heat evolved is not sufficient to kindle the hydrogen which is given off.

Soda (Na_2O) can be obtained by the action of sodium upon fused sodic hydrate.

Sodic Hydrate is now prepared on a large scale by the action of milk of lime on a solution of sodic carbonate, and the caustic liquid deposits at a certain concentration all the foreign salts present, in a solid state, so that they can be skimmed or strained off from the liquid soda. Sodic hydrate dissolves readily in water with evolution of heat, forming an intensely caustic liquid.

According to Dalton a solution of soda of 1.56 density contains 41.2 per cent. of anhydrous soda (Na_2O). At 1.36 it contains 26 per cent.; at 1.18 it contains 13 per cent.

Sodic Nitrate, or Chili saltpetre (NO_3Na), is obtained chiefly from dry districts of Chili, where it is present in large quantities on the surface of the soil. It is not used in the

manufacture of gunpowder, for it deliquesces in moist air. It is also more soluble in water than the potash salt.

216. Sodic Carbonate ($C O_3 Na_2$) is popularly called 'soda.' It used to be made from the ashes of sea-weeds. But the chief manufacture of soda is now by a process originally proposed by Leblanc, the introduction of which has constituted an era in the history of chemical manufactures.

The process consists of two stages: first, the preparation of sodic sulphate from common salt; secondly, the reduction of this sulphate ($Na_2 S O_4$) to sodic sulphide ($Na_2 S$) in presence of calcic carbonate. These compounds exchange metals, forming calcic sulphide and sodic carbonate.

The first operation is performed in large cast-iron pans about 12 inches deep in the centre and 9 feet diameter, each pan being the segment of a sphere. Each pan is roofed over by a similar cast-iron vessel with openings. A charge of 5 or 6 cwt. of salt is thrown into one of these pans, and about an equal weight of hydric sulphate, of the density 1.7, run in upon it. The bottom of the pan is heated by a fire until the decomposition of the salt by the sulphate is rather more than half complete—

$$S O_4 H_2 + Cl Na = S O_4 Na H + H Cl.$$

The hydric chloride which is formed is conducted to the bottom of a vertical flue full of pieces of coke, and while it rises upwards through this flue it meets water which is being poured in at the top, and which is trickling down over the coke. In this manner it is completely condensed by the water. When the action in the pan becomes sluggish, the charge is scraped out of it, and exposed to a higher temperature in a chamber of fire-brick, of which the bottom is heated by the flues from a furnace. Hydro-sodic sulphate, which was present in the charge, then decomposes the remainder of the salt; $S O_4 Na H + Cl Na = S O_4 Na_2 + Cl H$.

The sodic sulphate is then ground up with about an equal weight of chalk and half its weight (or rather more) of coal, and the mixture well melted by the flames of a reverberatory furnace, and after stirring is raked out to cool. It is then called 'black ball' or 'black ash.' The sodic carbonate has to be dissolved out from it as speedily as possible and crystallized, calcic sulphide remaining behind undissolved. Caustic soda is usually present; and this is separated from the crystals of the carbonate and evaporated to dryness for use in the caustic state, after the sodic sulphide and cyanide with which it is contaminated have been oxidized by fusion with sodic nitrate.

The common crystals of sodic carbonate contain ten molecules of water of crystallization ($C O_3 Na_2 (H_2 O)_{10}$); part of which evaporates in dry air, while the crystals crumble to powder, or effloresce, as it is called. Commercial sodic carbonate commonly contains a sulphate and chloride; occasionally a hyposulphite, sulphide, and cyanide. The best way to obtain pure sodic carbonate is to wash hydro-sodic carbonate, and decompose it by a dull red heat, driving off carbonic acid and water. Sodic carbonate has an unpleasant, bitter, and alkaline taste, and is strongly alkaline to test-paper. It is not soluble in alcohol.

Hydro-sodic Carbonate ($C O_3 Na H$) is usually made by exposing crystals of the carbonate to carbonic acid gas. It is far less soluble in water than the simple salt, and is decomposed gradually by boiling water, carbonic acid escaping.

A beautiful double carbonate containing potash and soda is easily obtained by dissolving the salts together in approximatively atomic proportions. The crystals consist of

$$C O_3 K Na (H_2 O)_6.$$

217. Sodic Chloride, or common salt ($Cl Na$), is the most plentiful of the soluble salts of soda. It constitutes

nearly three per cent. of the weight of sea-water, and in some climates is obtained by the spontaneous evaporation of sea-water in shallow enclosures by the sea-side. The crystals thus obtained are usually distinguished by the name 'bay-salt' from those prepared from subterranean sources. The evaporation is carried on until the remaining liquid has acquired a density of about 1.24. This mother liquid deposits sodic sulphate if artificially cooled to about $-17°C$, and by further evaporation can then be made to deposit nearly all the sodic chloride left in it while still hot.

The remaining liquid deposits on cooling crystals of a double chloride, containing potassium and magnesium; and from this double salt the magnesic chloride can be washed out by cold water, with a part of the potassic chloride, leaving the remainder of the potassic chloride in a pure state. This series of operations has been invented by M. Balard, aided in some particulars by M. Merle.

Sodic chloride is found in several parts of the world in large deposits in the earth, as so-called rock-salt, and in some localities in a state of great purity.

It crystallizes in cubes which contain no water of crystallization. A solution of salt saturated at the common atmospheric temperature (15°C) has a specific gravity of 1.204, and contains about 26.5 parts of salt. The addition of alcohol or of strong hydric chloride throws down some of the salt. Salt is volatilized to a considerable extent at a strong red heat, and in presence of moisture silica or alumina decomposes it, with evolution of hydric chloride.

It forms with platinic chloride a double salt ($Pt\,Cl_6\,Na_2$), which is soluble in alcohol, and sodium is thus separated from potassium.

Sodic chlorate cannot be separated from sodic chloride by crystallization, and for this reason potash is preferred as a base for holding chloric acid.

Salts of Soda are not precipitated by hydric fluo-silicate. The sodic sulphides are obtained by processes similar to those described for the potassic sulphides. Sodic hyposulphite ($S_2O_3Na_2$) is a salt considerably used by photographers for fixing, i. e. dissolving off the superfluous silver iodide from the developed plates. It can be obtained by dissolving sulphur in caustic soda by the aid of heat, and into the mixture of sodic hyposulphite and sulphide thus obtained leading sulphurous acid until the sulphide is decomposed. The salt usually crystallizes with five molecules of water—

$$S_2O_3Na_2(H_2O)_5.$$

218. Sodic Sulphate, or glaubers salt, is usually made by the action of hydric sulphate on common salt. It is most commonly met with in efflorescent crystals consisting of $SO_4Na_2(H_2O)_{10}$. It can also be obtained with $7\ H_2O$, and even in anhydrous crystals.

The solubility of sodic sulphate in water increases with rise of temperature up to 33°C, but a solution saturated at that temperature deposits some of its salt when the temperature is raised.

A solution of the salt, saturated at a high temperature and allowed to cool in a closed vessel, retains a larger quantity of salt in solution than it would take up at this lower temperature, and it is then called super-saturated. When such a solution is poured out of the vessel in which it had cooled down, it suddenly deposits a quantity of crystals with evolution of heat.

Sodic sulphate is not decomposed by heat.

Sodic Di-sulphate ($S^2O_7Na_2$) is formed by heating hydro-sodic sulphate to a dull red heat, until fumes of sulphuric acid begin to make their appearance. Two molecules of the double salt eliminate one molecule of water, and form one molecule of the acid sulphate—

$$2\ SO_4NaH = S^2O_7Na_2 + H_2O.$$

At a strong red heat the salt is decomposed, leaving neutral sodic sulphate.

The double sulphate containing sodium and hydrogen ($H\,Na\,S\,O_4$) has considerable resemblance to the corresponding double salt containing potassium, and is decomposed with even greater readiness by water or alcohol, into hydric sulphate and the neutral sulphate.

219. Sodic Phosphate occurs commonly in the form of the double salt with hydrogen, containing one atom of hydrogen and two of sodium. The crystals of this hydro-di-sodic phosphate contain 12 molecules of water of crystallization—

$$P\,O_4\,Na_2\,H\,(H_2\,O)_{12}.$$

This salt is not unfrequently called rhombic phosphate, from the circumstance of its occurring in rhombic prisms. It is obtained by adding sodic carbonate to a solution of hydric phosphate or of tetra-hydro-calcic di-phosphate. The salt is slightly alkaline to test-paper. The crystals dissolve in about four times their weight of cold water, or half that quantity of boiling water. When the salt is heated to redness it loses all its hydrogen as water, leaving an acid phosphate of the composition $P_2\,O_7\,Na_4$, which is considerably less soluble in water than the rhombic salt. This salt is commonly called pyro-phosphate, but its systematic name is tetra-sodic di-phosphate. Hydric nitrate decomposes common hydro-di-sodic phosphate, forming sodic nitrate, and replacing one atom of sodium in the salt by one of hydrogen. The addition of alcohol to such a mixture precipitates a salt acid in its reactions—

$$P\,O_4\,Na_2\,H + N\,O_3\,H = N\,O_3\,Na + P\,O_4\,Na\,H_2.$$

Caustic soda added to a solution of the rhombic phosphate decomposes it by removing its hydrogen, and replacing it by an atom of sodium—

$$P\,O_4\,Na_2\,H + H\,O\,Na = P\,O_4\,Na_3 + H_2\,O.$$

This sodic phosphate is strongly alkaline, and is decomposed even by carbonic acid, with reproduction of the rhombic salt.

When sodic phosphate is mixed with a molecule of ammonic chloride in presence of little water, a triple salt called microcosmic salt is formed, containing sodium, ammonium, and basic hydrogen—

$$P O_4 Na_2 H + Cl N H_4 = P O_4 Na (N H_4) H + Cl Na.$$

This salt leaves at a red heat a residue called sodic metaphosphate—$P O_4 Na (N H_4) H - N H_3 - H_2 O = P O_3 Na$.

Boracic acid forms a great many double salts with soda and water. Borax is the name given to the common salt $B_4 O_7 Na_2 (H_2 O)_{10}$, which is made by dissolving boracic acid in sodic carbonate. Borax is alkaline to test-paper.

220. Di-sodic Silicate is now manufactured for the preparation of artificial stone, and also as a constituent of some kinds of soap. Caustic soda is heated with flint stones in a high-pressure boiler, which is revolving on a horizontal axis, so that the contents are continually agitated. It is usually sold at a density of about 1.5. When made by fusion of silica with sodic carbonate, it contains acid and base in proportions corresponding to the compound $Si O_3 Na_2$. This compound has been obtained in crystals from an aqueous solution. A solution of this salt dissolves silica, forming a compound which contains silica and soda in proportions corresponding nearly to a tetra-silicate ($Si^4 O_9 Na_2$).

Double silicates, containing soda and lime, are the chief constituents of common window and bottle glass. The presence of the calcic silicate, or of some such salt, is needed to prevent the alkaline silicate from dissolving in water.

Glasses made for different purposes present some differences of composition. Thus, the hard glass used for operations in which a very high temperature is resorted to, consists of potassic silicate combined with calcic silicate.

Glass for lustres, or for optical instruments, in which considerable dispersive power is needed, is made of an alkaline silicate combined with plumbic silicate, and is usually distinguished by the name of 'flint-glass.' The composition of very few kinds of glass agrees with any exact formula, as they are to some extent mixtures in various proportions of definite compounds; but the following formulæ represent very nearly a couple of the more important varieties, which may serve as samples—

$(Si\ O_2)_4\ (Ca\ O)\ (Na_2\ O)$, French window glass,

$(Si\ O_2)_6\ (Pb\ O)\ (K_2\ O)$, English flint glass.

Aluminium partially replaces sodium in many of our common kinds of glass, and oxide of iron is usually present.

For the common kinds of glass the materials are melted together in open pots made of very infusible clay; but flint glass is melted in pots which open only to the air of the room in which the furnace is contained, so that no ashes or products of imperfect combustion can reach the glass. This precaution is necessary to protect the flint glass from the blackening which it would undergo by contact with carbonic oxide or smoke.

When the glass has been moulded into the proper shape, it has to undergo a process of baking, called annealing, at a temperature intermediate between that of the glass pot, and that of the air in which the glass vessel is to be kept. The effect of this process is to allow the particles of the viscid material time to contract gradually and uniformly, to the volume corresponding to lower temperatures. Suddenly-cooled glass is liable to break into fragments, or even into powder, when its surface is even scratched; and imperfectly-annealed glass is liable to break, far more easily than glass which has been well annealed. Some kinds of glass are liable to become opaque like earthenware if long exposed to a high temperature. This process of devitrification is

attributed to a crystallization of components of the glass. The material thus formed is called Reaumur's porcelain.

Glass is coloured by various metallic oxides which are dissolved in it. Thus, the green colour of bottle glass is due to ferrous oxide, and ferric oxide imparts a reddish yellow colour. Green colours are given by cupric oxide, or by chromic oxide. Cuprous oxide gives the intense red colour which is so well known. Uranic oxide forms a fluorescent yellow glass. Gold and stannic oxide give a red colour, and yellow is obtained by silver oxide mixed with antimonic oxide. Glass is coloured blue by oxide of cobalt.

Neutral sodic salts are precipitated by a solution of potassic antimoniate, the sodic antimoniate being very nearly insoluble in water. The precipitate, after removal of its water of crystallization by heat, has the composition

$$Sb_2 O_7 Na_2 H_2.$$

221. Lithium (Li = 7; sp. gr. 0.59; melting-point, 180°). This metal occurs as a basic constituent of many minerals, but it does not form a large percentage of any of them. Triphylline or petalite are the minerals usually employed for its preparation. The metal is obtained from its fused chloride by electrolysis.

Lithia ($Li_2 O$) is a strong base, similar in its general reactions to potash or soda. Its hydrate (H O Li) is not decomposed by heat.

Lithic carbonate is but slightly soluble in water. On the other hand, the chloride forms with platinic chloride a double salt ($Pt Cl_6 Li_2$), which is even more soluble in water and in alcohol than the corresponding salt of sodium.

Lithic phosphate ($P O_4 Li_3$) is almost insoluble in water, but readily soluble in hydric salts. This salt frequently contains sodium in place of a part of its lithium.

Lithium is best detected by the beautiful crimson colour which its chloride imparts to flame.

Lithic chloride is soluble in a mixture of alcohol and ether, and is thus separated from sodic chloride, which is not soluble in that mixture.

222. Rubidium and **Cœsium** are metals of the same family as the alkali metals. Both these have been discovered within the last few years by the peculiar lines of light which their volatile compounds give in the spectrum—rubidium giving a red line and cœsium a couple of blue lines.

Rubidium forms a platinum salt less soluble in water than the platinum salt of potassium; and cœsium forms a still less soluble platinum salt. It is by the aid of these salts that compounds of these metals are separated from salts of potassium, with which they usually occur.

ORGANIC CHEMISTRY.

CHAPTER XXXIV.

223. Many acids, bases, and neutral compounds, are usually obtained from plants or animals, to whose organism they belong. Thus, citrates are prepared from lemons, tartrates from grapes, formiates from ants, albumen or gelatin from animals; sugar, starch, gum, resin and essential oils, &c. from plants; quinine, morphia, &c. also from plants. These substances were called 'organic,' to denote their origin in living organisms.

Other substances are made from materials derived from animals or plants, and not from mineral materials, such as those which are employed for the formation of inorganic compounds. Thus oxalates are usually made from starch or from woody fibre, and formiates from the oxalate; alcohol is made from sugar, and olefiant gas is made from alcohol; acetates are also made from sugar, and acetone or marsh gas is made from an acetate; lactates or butyrates are made from sugar; glycerine is made from fat, and propylene is made from glycerine. The term 'organic' has been extended to these bodies, inasmuch as they come from animals or plants, although not directly like the first-named class, but indirectly.

All of these bodies, whether themselves extracted from vital organisms, or derived from others so extracted, are found to contain carbon, and most of them contain hydrogen and oxygen also. Not a few contain nitrogen, in addition to carbon, hydrogen and oxygen. All of them are destroyed

by the action of a high temperature; for they pass over into other compounds, usually termed products of destructive distillation, which do not on cooling return to the state of combination in which they occurred in the organic compounds.

Thus wood when distilled yields a mixture of various gaseous compounds, accompanied by tarry matter and acetates, acetone, methylic alcohol, benzole, &c., while carbon is left behind in the retort in which the wood was heated; and these various products do not on cooling reunite to form the woody fibre from which they were made.

Some mineral substances are, no doubt, also decomposed by heat, forming products of decomposition which are unable to reunite on cooling so as to reproduce the compound whose decomposition gave rise to them.

Thus pyrites gives off when heated some of the sulphur contained in it, and the lower sulphide which is left does not combine with the free sulphur to reproduce pyrites. Silver oxide is decomposed by heat into metallic silver and oxygen, and these products do not recombine on cooling.

Ammonia is decomposed by a strong heat into a mixture of free nitrogen and hydrogen, which does not recombine on cooling.

On the other hand, the greater number of decompositions and other changes of mineral bodies, effected by the action of rise of temperature, are reversed by mere cooling. Thus, common phosphoric acid (trihydric phosphate) decomposes when heated, forming water and hydric meta-phosphate; but the two bodies recombine if left together in the cold. Calcic hydrate is decomposed by heat into lime and water, but the products unite again to form the original hydrate as soon as they are brought together. Hydro-sodic sulphate is decomposed by heat into sodic sulphate and hydric sulphate, but if the products be left together in the cold, they reunite

to form the original double salt. Hydric sulphate itself is believed to decompose on evaporation into water and acid, but these bodies combine again to form the original sulphate during the process of cooling. Mineral compounds are expanded by heat, and many are transformed by rise of temperature into liquids, and these in their turn, by still further heating, into vapours; but on cooling, the vapour contracts and condenses to the original liquid; this, in its turn, returns on sufficient cooling to the original solid state.

The difference between organic and inorganic compounds with respect to heat may be thus summed up: That whereas all organic bodies are decomposed by heat, the great majority of mineral bodies are not permanently decomposed by it.

224. Organic molecules are more complicated in their structure than mineral molecules, and chemists have felt the necessity of imagining radicals to explain the constitution of organic bodies, before they needed such aid in explaining the more simple compounds of mineral chemistry. This important difference is embodied in Liebig's dictum — 'Organic chemistry is the chemistry of compound radicals.' Nothing indeed is more remarkable than the extension which the theory of radicals has undergone of late years, side by side with the extension of our knowledge of organic bodies, and organic bodies are only explained by shewing what radicals they contain. If compound radicals belonged only to organic bodies, this circumstance would afford us a very simple distinction between organic and mineral chemistry, but the distinction is by no means absolute.

225. In organic chemistry we have mainly to do with compound radicals which act like elements; whereas in mineral chemistry we meet with elementary bodies uniting in their individual capacity, as well as groups of elements which act like elementary atoms. Thus metallic oxides,

sulphides, chlorides, bromides, iodides, nitrides, phosphides, find no parallel in organic chemistry, while metallic nitrates, sulphates, phosphates, &c. may be compared to the metallic acetates, tartrates, citrates. In the formula $Ag\,N\,O_3$ for argentic nitrate we may consider that $N\,O_3$ is a radical, just as much as in argentic acetate $Ag\,(C^2\,H_3\,O_2)$ the group $C^2\,H_3\,O_2$; for when a molecule of the nitrate is decomposed by potassic chloride, the silver takes up an atom of chlorine in lieu of its atom of the radical $N\,O_3$, and when the acetate is decomposed by potassic chloride, the radical $C^2\,H_3\,O_2$ changes places with chlorine.

So also a sulphate $H_2\,S\,O_4$ undergoes double decompositions analogous to those of a succinate $H_2\,C^4\,H_4\,O_4$, and $S\,O_4$ is the divalent radical of the sulphate just as much as $C^4\,H_4\,O_4$ is that of the succinate. $H_2\,S\,O_4$ may be compared to hydric chloride, or, in other words, represented on that type, by considering it as formed from two molecules of chloride 2 H Cl, by removing the two monad chlorine atoms and replacing them by the dyad $S\,O_4$; and in like manner the succinate may be represented on the chloride type by calling it two molecules of the chloride, in which the dyad $C^4\,H_4\,O_4$ replaces two chlorine monads.

For many purposes it is more convenient to represent the arrangement of the elements of these molecules on the type of water H O H, and they must then be considered as containing radicals differing from these by having two atoms less of oxygen in their composition. Thus the sulphates viewed on the water-type contain the dyad $S\,O_2$, which replaces two atoms of hydrogen in two molecules of water; half of it being in the place of an atom of hydrogen which has left one molecule of water, the other half of it being in the place of an atom of hydrogen which has gone out from the second molecule of water.

The two molecules may for convenience be written

thus: H O H H O H, and hydric sulphate has got the dyad $S O_2$ in the place of the two middle atoms of hydrogen, thus—H O ($S O_2$) O H. In like manner the succinates contain the dyad $C^4 H_4 O_2$ in the place of two atoms of hydrogen, one from one molecule of water, one from another: thus—H O ($C^4 H_4 O_2$) O H.

In salts consisting of organic acids combined with metallic bases, these latter are really the inorganic part of the compound; and in like manner organic bases combine with acid hydrogen salts, such as the chloride, sulphate, &c., but in these last-named salts the really organic part is the radical which acts the part of basic metal.

Thus the radicals methyle ($C H_3$), ethyle ($C^2 H_5$), propyl ($C^3 H_7$), and others of this series, are really the hydrogens of organic chemistry; and their salts, such as methylic chloride (Cl $C H_3$), vinic chloride (Cl $C^2 H_5$), &c., correspond to the mineral chlorides containing monovalent metals.

Other radicals, such as ethylene ($C^2 H_4$), propylene ($C^3 H_6$), &c., are dyads, like zinc, barium, &c., and form chlorides, bromides, nitrates, &c., of which each molecule contains two atoms of chlorine, bromine ($N O_3$), &c. (such as $C^2 H_4 Br_2$, $C^3 H_6 Br_2$, like $Zn Br_2$ or $Ba Br_2$). Nor does the analogy stop here, for there are also trivalent and tetravalent radicals, and others of still higher equivalence in organic chemistry, corresponding to trivalent antimony, tetravalent tin, &c.

Glycerine affords an illustration of an organic compound containing a trivalent radical, replacing three atoms of hydrogen in three atoms of water. Its empyrical formula is $C^3 H_8 O_3$, and its reactions and decompositions prove it to contain the triad glycerile $C^3 H_5$, thus $(H O)_3 C^3 H_5$. Erithrite is a compound of a tetravalent radical of the composition $C^4 H_6$. This radical replaces four atoms of hydrogen in four molecules of water, forming erithrite $C^4 H_6 (O H)_4$. The nitrate of this basic body is formed by replacing the

hydrogen, not belonging to the radical but to the water, by the radical NO_2. Its formula is $C^4H_6O_4(NO_2)_4$. Just as platinic nitrate corresponds to the platinic hydrate $Pt(OH)_4$, the hydrogen being replaced atom for atom by NO_2, forming $PtO_4(NO_2)_4$.

On the other hand, organic chemistry abounds in compounds of basic radicals with chlorous radicals, such as methylic acetate $C^2H_3O(OCH_3)$, vinic succinate $C^4H_4O_2(OC^2H_5)_2$, glycollic acetate $C^2H_4O_2(C^2H_3O)_2$, glycollic succinate $C^2H_4O_2(C^2H_4O_2)$, acetine $C^3H_5O_3(C^2H_3O)_3$, &c.; and these bodies, built up entirely of compound radicals, are most characteristic of organic chemistry, and entitle that branch of the science to the designation which Liebig gave it.

It will be understood from these few examples that the constitution of organic compounds is more complicated than that of mineral compounds, and that organic compounds present greater varieties of property than mineral bodies. Thus alcohol is in organic chemistry the representative of water in mineral chemistry; but, instead of being the only body of its kind, alcohol is one term of a numerous series, varying in composition from CH_4O to $C^{30}H_{62}O$, and presenting properties as different as their composition. Some alcohols are volatile fluids which have not been frozen by the greatest artificial cold to which they have been subjected, whereas others are solid wax-like bodies, fusible only at temperatures approaching the boiling-point of water. $C^{27}H_{56}O$ melts at 97°.

226. The formation of most organic compounds—such as sugar, woody fibre, quinine, albumen, &c.—is effected in the organism of growing plants under the influence of sunshine; and chemists for some time did nothing more than extract these products from vital organisms, and break them up into the simple products, carbonic acid, ammonia,

and water, from the elements of which they were built up, or break them up less completely into products of simpler constitution than themselves, yet more complex than the ultimate products of combustion. Thus by the action of hydric nitrate on sugar ($C^6H_{10}O_5$) carbonic acid and water are obtained by a process of combustion at the expense of the oxygen of the acid—

$$C^6H_{10}O_5 + 12\,HNO_3 = 6\,CO_2 + 12\,HNO_2 + 5\,H_2O.$$

But by moderating the action of the acid, and using less of it, oxalate was prepared—

$$C^6H_{10}O_5 + 9\,HNO_3 = 3\,C^2O_4H_2 + 9\,HNO_2 + 2\,H_2O.$$

By using still less of the oxidizing agent, tartrate is obtained, together with a smaller quantity of oxalate—

$$C^6H_{10}O_5 + 6\,HNO_3 = C^4H_6O_6 + C^2O_4H_2 + \\ + H_2O + 6\,HNO_2.$$

And by moderating still further the oxidizing action, the hydrate of a substance called saccharic acid is obtained—

$$C^6H_{10}O_5 + 3\,HNO_3 = C^6H_{10}O_8 + 3\,HNO_2.$$

This saccharate is easily oxidized to tartrate, and thence to oxalate; and hydric oxalate in its turn is easily oxidized still further to form carbonic acid—

$$C^6H_{10}O_8 + 6\,HNO_3 = 3\,C^2O_4H_2 + 6\,HNO_2 + 2\,H_2O;$$
$$C^2O_4H_2 + HNO_3 = 2\,CO_2 + HNO_2 + H_2O.$$

Saccharates, tartrates, and oxalates, were classed among organic compounds because we had only made them by such processes as the partial decomposition of sugar; and the oxalate was not considered the less entitled to rank among organic compounds from the fact that it was often made from the acid juice of the sorrel.

227. Later researches, however, shewed that oxalates can be built up artificially—without the materials of any plants, and from inorganic materials. Thus nitrogen gas passed over a hot mixture of carbon and sodic carbonate forms

sodic cyanide (Na C N), while carbonic oxide escapes. From this sodic salt it is easy to prepare mercuric cyanide; and this when heated gives off cyanogen gas. Cyanogen dissolves readily in water, and the two compounds gradually decompose one another, forming amongst other products ammonic oxalate—

$$2\,C\,N + 4\,H_2\,O = C^2\,O_4\,(N\,H_4)_2;$$

from which hydric oxalate is liberated by a mineral hydric salt.

By the action of sodium on oxalic ether Löwig has obtained a compound, which he calls desoxalate; and a desoxalate breaks up into one kind of tartrate and carbonic acid.

Alcohol is another product classed among organic bodies from the fact of its being obtained by a partial breaking up of sugar. For under the influence of growing yeast grape sugar breaks up partly into carbonic acid and alcohol—

$$C^6\,H_{12}\,O_6 = 2\,C^2\,H_6\,O + 2\,C\,O_2.$$

But Berthelot has shewn that alcohol can be built up artificially from its elements. He first makes acetylene ($C^2\,H_2$) by discharging a galvanic battery in an atmosphere of hydrogen by carbon points. This acetylene he combines with copper, and he then brings it in contact with nascent hydrogen, thereby forming ethylene ($C^2\,H_4$); and ethylene he combines with oil of vitriol, forming the compound $C^2\,H_6\,S\,O_4$, from which alcohol is liberated by dilution with water and distillation.

Urea is another compound first obtained only from an organic source, but subsequently prepared from mineral materials. The number of organic compounds which we have learnt how to build up by inorganic processes is already very great, and additions are constantly being made to it; so that it is no longer customary to apply the term 'organic' only to those compounds which are derived directly or indirectly from plants or animals. Some com-

pounds which were originally considered as organic are now usually studied among mineral compounds, and there seems a tendency in inorganic chemistry to continue this encroachment on the domain of organic chemistry; but the general distinction between the two parts of the science is not the less real nor the less marked.

228. The formation of complex molecules, such as sugar, albumen, &c., together with free oxygen, from carbonic acid, ammonia, and water, are, however, not the only results of the vital processes of plants; for there are processes of partial breaking up of complex organic molecules into less complex molecules by the agency of growing plants, analogous to the cases of partial breaking up which are effected by artificial means. Thus the fermentation of sugar is a transformation of a complex molecule, into a variety of simpler molecules, of which the best known are alcohol, carbonic acid, glycerine, hydric succinate; and this process has been shewn by the admirable investigations of Pasteur to be due to the growth of the so-called yeast or ferment, a plant which lives upon sugar, and gives off these simpler molecules by decomposition of the sugar. In like manner the formation of acetate from alcohol or from sugar in contact with air is effected by another plant, called mycoderma aceti.

Another ferment, called penicillium glaucum, transforms a mixture of chalk and sugar into a lactate; and the lactate thus formed is in its turn decomposed by another process of fermentation, giving rise to a butyrate, carbonic acid, hydrogen gas, &c. Under certain conditions sugar is broken up by a process of fermentation into mannite and a kind of gum. As far as researches have gone as yet into this most important class of phenomena, it would appear as if a great variety of elementary plants and infusoriæ were capable of effecting transformations of organic bodies by processes of

fermentation or putrefaction, and that each little organism has a sphere of action peculiar to itself, being capable of decomposing particular organic compounds only. Thus calcic tartrate in presence of atmospheric oxygen serves as food for monads, bacteriums, &c., which evolve carbonic acid. If, however, oxygen be excluded from the mixture, these infusoriæ die off, and vibrios are developed from germs in the liquid, and grow during the decomposition of the tartrate, and no doubt at its expense.

229. Water containing sugar, ammonic salts, and the ashes of yeast, soon becomes inhabited by various lower forms of living beings if merely exposed to the atmosphere. In like manner other mixtures capable of undergoing fermentation are found to contain infusoriæ and fungi, &c., after exposure to the air for some time.

On the other hand, Pasteur has shewn that all germs of organic life in such a mixture are destroyed at a temperature of about 130°, and that the liquid may then be kept for any length of time in a closed vessel without undergoing fermentation or putrefaction of any kind.

Moreover, no fermentation or putrefaction is started in such a liquid by air which has been passed through a red-hot tube, or which has been strained by passing through a tube filled by a porous plug of cotton-wool or of gun-cotton. In both of these cases the air is freed from all germs or seeds, &c., and it is found incapable of setting up the process of fermentation or of putrefaction in any liquid previously deprived of all germs of organic beings. On the other hand, it has been shewn by Pasteur that the dust strained off from the air by the cotton is sufficient to set up a process of decomposition of any suitable liquid, and that infusoriæ and fungi, &c., are found to be in active growth in the liquid during the whole continuance of its fermentation. By examination under the microscope the dust was moreover

found to contain, besides the various earthy and woody particles, &c., little cellular masses precisely similar in appearance to the spores of fungi, &c.

In the course of these investigations it was found that the germs of animal life contained in milk (an alkaline liquid) are not destroyed by boiling at the ordinary atmospheric pressure. They were, however, completely destroyed by boiling the milk at a pressure of about 1140 millimetres (1.5 atmospheres), and the milk could then be kept for an indefinite time in a closed vessel without undergoing any decomposition.

230. The distinction between direct and indirect combination is one of the most important evidences of the existence of atoms, apart from any quantitative considerations.

Water is a compound of two atoms of hydrogen and one atom of oxygen, but how are the two atoms of hydrogen connected? Clearly, not directly with one another; for if the oxygen be replaced by an equivalent quantity of chlorine, the two atoms of hydrogen do not remain together, but each one passes off in combination with an atom of chlorine. One of the atoms of hydrogen in water may be replaced by an atom of potassium, the well-known body, potash, being produced; and this compound affords another proof that the two monad atoms are not united directly with one another, for no compound of hydrogen and potassium alone is known, and yet in potash they are so firmly held together, that they remain in union even at a red heat. From such considerations as these, it is concluded that the atom of oxygen binds together the two atoms of hydrogen in water, and the atoms of hydrogen and potassium in potash. The same thing may be observed in numerous organic compounds, and it is found that those atoms which are only indirectly united with the carbon possess different

properties to those which are directly united with it. Thus the two compounds vinic alcohol and methylic ether have the same empirical formula, $C^2 H_6 O$; but the reactions of the former shew that it is to be represented as having five atoms of hydrogen united directly with the carbon, and the sixth atom united indirectly with it by means of the oxygen; while those of the latter body indicate that the whole of the six atoms of hydrogen are united directly with the two atoms of carbon. Thus in vinic alcohol $H O C^2 H_5$, if the oxygen be replaced by an equivalent quantity of chlorine, half of the chlorine remains in combination with the group $C^2 H_5$, while the other half enters into combination with the sixth atom of hydrogen. In methylic ether, however, $H_3 C O C H_3$, under similar conditions the chlorine is equally divided between the two groups of $C H_3$.

231. In zinc-iodo methide, $I Zn C H_3$, the atoms of carbon and iodine are bound together by an atom of zinc. When this compound is acted upon by methylic iodide, $I C H_3$, the atoms of carbon and iodine are separated, the two atoms of iodine entering into combination with zinc, while the two atoms of carbon unite with each other—

$$I Zn C H_3 + I C H_3 = H_3 C C H_3 + Zn I_2.$$

From the state in which the carbon exists in methylic iodide, partly in combination with hydrogen, and partly with iodine, it changes in the compound $H_3 C C H_3$, to being partly combined with hydrogen and partly with carbon. The introduction of this principle, that is, the union of atoms of the same element, is very important, as it enables many facts to be explained which would otherwise be anomalous. For instance, in the series of compounds of carbon and hydrogen, $C^2 H_2$, $C^2 H_4$, $C^2 H_6$, the same amount of carbon is united with different amounts of hydrogen, this being explained by the fact that the carbon is partly united with carbon, and partly with hydrogen. Various reactions

in which these bodies take part shew that the two atoms of carbon do not separate from one another, but remain firmly in combination.

232. In ordinary notation, when any elements are combined, the fact is denoted by the symbols for those elements being placed in juxtaposition. In algebra, when two symbols are multiplied together, which is the sign of combination, they are placed side by side, as $a\,b = a \times b$, and if the symbols be the same, a number indicating how many symbols are multiplied is written above, as an exponent, thus: $a \times a = a\,a = a^2$. In the same manner, when two or more atoms of the same element are combined with one another, the number of atoms so united will be written above the symbol, as an exponent, thus:

$$H\,H = H^2;\quad P\,P\,P\,P = P^4.$$

233. The molecule of hydric chloride consists of one atom of hydrogen combined with one atom of chlorine, and is represented by the formula H Cl. Experiment shews that the atom of hydrogen in this molecule can be replaced by one atom of potassium, and that this is the only proportion in which it can be replaced by potassium. Each atom of hydrogen in marsh gas also, can be replaced by an atom of chlorine, but neither more nor less than one atom of chlorine can replace one atom of hydrogen. The following formulæ represent the products of the successive replacement of hydrogen by chlorine in marsh gas—

$$C\,H_4;\quad C\,H_3\,Cl;\quad C\,H_2\,Cl_2;\quad C\,H\,Cl_3;\quad C\,Cl_4.$$

It is important to notice that one atom of chlorine can either combine with, or replace, one atom of hydrogen.

To replace the oxygen in one molecule of water H O H, two atoms of chlorine are necessary, and it must be noticed at the same time, that in the molecule of water *one* atom of oxygen is combined with *two* atoms of hydrogen. If the converse reaction be attempted, that is, the replacement of

chlorine in hydric chloride by oxygen, it will be found that two molecules of hydric chloride, containing two atoms of chlorine, must be taken, one atom of oxygen taking the place of the two atoms of chlorine.

In ammonia, one atom of nitrogen is combined with three atoms of hydrogen; and in no compound is nitrogen known to replace or combine with less than three monovalent atoms like hydrogen.

In marsh gas an atom of carbon is combined with four monovalent hydrogen atoms, one atom of carbon replacing four atoms of chlorine in four molecules of hydric chloride.

Thus the atom of oxygen being capable of replacing or combining with two atoms of a monovalent element, is said to have an ATOMIC VALUE of two. Nitrogen, being capable of replacing or combining with three monovalent atoms, has an atomic value of three; and carbon, from similar considerations, has attributed to it the atomic value of four.

Like oxygen, the three elements sulphur, selenium, and tellurium, form compounds containing in the molecule two atoms of hydrogen combined with one atom of one of these elements. From this circumstance they are considered, like oxygen, as belonging to the group of divalent elements. Nitrogen also has its analogues in the elements phosphorus, arsenic, and antimony, all of which are trivalent in some compounds, and pentavalent in others. Silicon, tin, and titanium, resemble carbon in the compounds they form, and are thus classed with it as tetravalent elements.

CHAPTER XXXV.

234. Alcohol, sometimes called vinic alcohol (C^2H_6O= 2 vols.; sp. gr. at 0° is 0.818, at 15° it is 0.7996; boiling-point, 78.4°). When mixed with a small quantity of water, this compound is called spirits of wine, and the pure alcohol is sometimes distinguished by the name 'absolute alcohol.'

By distillation of a fermented liquid a mixture of water and alcohol can be obtained, containing as little as about 10 per cent. of water; but this mixture cannot be separated by further distillation, as the two liquids go over together in these proportions without any further division. In order to dry the alcohol further, the mixture may be distilled over dry potassic carbonate, but in order to dry it completely it ought finally to be mixed in a retort with its own weight of quick-lime in lumps, allowed to stand on the lime for several days (the retort being closed by a cork), and finally distilled off. The first portions collected contain the moisture of the apparatus, and should accordingly be rejected. Alcohol thus prepared sometimes contains volatile oils, which were contained in the materials from which the alcohol was made, or produced during the fermentation. To purify it from these admixtures it should be shaken up with animal charcoal before it is dried. Alcohol is liable to become acid by distillation in contact with air, by absorbing oxygen. It is also frequently accompanied by ammonia from the fermented liquid.

235. It mixes with water in all proportions, and the

mixtures occupy a smaller volume than the alcohol and water occupied previous to mixing.

Tables have been constructed from careful experiments shewing the density of mixtures of alcohol and water in various proportions, and the usual way of ascertaining how much alcohol is contained in a particular sort of wine or beer, &c., is to distil a known quantity of the liquid, say 500 cubic centimetres, collecting carefully all that comes over until two-thirds of the liquid are distilled off. This distilled liquid (or distillate) is accurately measured, and its specific gravity is then determined at the temperature named in the table of specific gravities, by an aræometer, or, better still, by a specific-gravity flask. A reference to the table then shews how much alcohol there is in one hundred parts of a mixture of the observed density, and from this the operator calculates how much must have been in his measured distillate, and thence how much in the 500 cubic centimetres of wine.

The term 'proof spirit' is still in use in this country among those who are not sufficiently aware of the value of the centesimal manner of describing the composition of mixtures in use among scientific persons. The strength of spirits of wine used to be tested by moistening some gunpowder with it, and then setting fire to the spirits. If the spirits of wine fired the gunpowder, it was said to be 'over proof;' but if it contained too much water to produce that effect, it was called 'under proof.' Proof spirit is now defined by law as containing 49.24 per cent. of alcohol. Every half per cent. of alcohol above this proportion is called one degree 'over proof.'

236. When alcohol is present in small quantity in water, it can be detected by saturating the mixture with potassic carbonate, when the alcohol makes its appearance as an oily stratum floating on the aqueous solution of the carbonate.

The separation is the result of the fact that the carbonate is insoluble in alcohol, but exceedingly soluble in water.

Alcohol does not dissolve any mineral salts which are insoluble in water; and, as Miller has pointed out, it dissolves nearly all deliquescent salts, such as calcic chloride, nitrate, &c., and very few efflorescent salts, such as sodic carbonate, sulphate, &c.

Alcohol dissolves the elementary gases, oxygen, hydrogen, nitrogen; also nitrous oxide, ammonia, carbonic oxide, carbonic acid, and the gaseous hydrocarbons, to a considerably greater extent than water dissolves them.

Caustic potash or soda dissolves to a considerable extent in alcohol, and when exposed to the air such a solution becomes yellow or brown by absorbing oxygen, and forming a so-called resin of aldehyde. Potassium or sodium also dissolves in alcohol very rapidly, giving off hydrogen with considerable rise of temperature. The solution thus obtained contains a compound called potassic (or sodic) ethylate ($K C^2 H_5 O$), which remains behind in the solid state when the alcohol is distilled off from it.

Potassic ethylate is an intensely alkaline compound, possessing great analogy with potassic hydrate. It is present in the liquid obtained by dissolving potassic hydrate in alcohol, being formed by an interchange of the hydrogen of the hydrate with the group $C^2 H_5$, called ethyle, of the alcohol—

$$K(H)O + H(C^2 H_5)O = K(C^2 H_5)O + H H O.$$

When alcohol is dropped upon molten potassic hydrate an evolution of hydrogen gas takes place, and potassic acetate is formed—

$$C^2 H_6 O + K H O = 2 H^2 + K C^2 H_3 O_2.$$

Oil of vitriol mixes with alcohol in all proportions, evolving considerable heat. When a mixture of the two

liquids is heated, the alcohol breaks up chiefly into ether and water—

$$2\,C^2H_6O = C^4H_{10}O + H_2O,$$

if the sulphate be present in the proportion of two parts by weight to one of the alcohol. When as much as four parts of the sulphate are present to one of alcohol, the decomposition which takes place on heating is chiefly into olefiant gas and water; $C^2H_6O = C^2H_4 + H_2O$.

237. Alcohol burns in the air with a pale blue flame. Its vapour requires three times its own volume of oxygen for combustion, as can be seen by the equation —

$$\underset{2\text{ vols.}}{C^2H_6O} + \underset{6\text{ vols.}}{O^6} = \underset{4\text{ vols.}}{2\,CO_2} + \underset{6\text{ vols.}}{3\,H_2O}.$$

When its vapour, mixed with an insufficient quantity of air for its complete combustion, is allowed to pass over a warm surface of metallic platinum, it undergoes a partial combustion, forming an acrid and pungent volatile compound.

Even in presence of water alcohol is readily oxidized to a limited extent. A red solution of potassic dichromate and hydric sulphate is very speedily changed to an emerald green colour by the addition of alcohol, and a peculiar sickly odour is perceived at the same time, owing to the formation of a body called aldehyde, consisting of C^2H_4O, or a molecule of alcohol from which two atoms of hydrogen have been burnt away. At the same time with aldehyde there is usually hydric acetate formed ($C^2H_4O_2$), by the addition of an atom of oxygen to the elements of the aldehyde. Alcohol is entirely decomposed by passing its vapour slowly through a red-hot tube, a mixture of carbonic oxide, olefiant gas, marsh gas, hydrogen, besides several condensable hydrocarbons, being formed.

The action of monobasic hydrogen salts upon alcohol

consists in forming water and a salt containing the radical C^2H_5 in place of the hydrogen of the original hydrogen salt. Thus hydric chloride forms water and ethylic chloride—

$$HC^2H_5O + HCl = HHO + C^2H_5Cl.$$

Hydric iodide, in like manner, forms water and ethylic iodide—

$$HC^2H_5O + HI = HHO + C^2H_5I.$$

Hydric nitrate forms water and ethylic nitrate—

$$HC^2H_5O + HNO_3 = HHO + C^2H_5NO_3.$$

238. These reactions are precisely similar to those which take place between potassic hydrate and the same hydrogen salts, the group C^2H_5 from alcohol forming a salt as potassium does in its corresponding reactions. Thus writing K for C^2H_5 in the last equation we have the double decomposition between potassic hydrate and hydric nitrate, forming water and potassic nitrate—

$$HKO + HNO_3 = HHO + KNO_3.$$

Throughout all the reactions among its compounds the group C^2H_5 exhibits this analogy with a monovalent metal, and it is accordingly considered as a monovalent organic radical, that is, as an organic radical of which the atom as represented by the formula C^2H_5 is capable of replacing one atom of hydrogen in its various salts.

According to this view, the constitution of alcohol is explained by comparing it to water. If a molecule of water, H H O, were to lose one of its atoms of hydrogen and to take up an atom of ethyle in the place of that hydrogen, it would be transformed into alcohol. We shall see that alcohol is easily made by this process. It is important, moreover, to observe that inasmuch as the molecule of alcohol and the molecule of water each occupies two volumes in the state

of vapour, the atom of ethyle takes exactly the space vacated by the atom of hydrogen which it replaces—

$$H\,H\,O = 2 \text{ vols.} \quad H\,(C^2\,H_5)\,O = 2 \text{ vols.}$$

When alcohol or any other substance is thus represented on the water-type, it often becomes necessary to distinguish between the hydrogen of the ethyle and the hydrogen of the original type (water). The term 'typical hydrogen' is used to denote hydrogen remaining from the water, in any compound belonging to the water type; or more generally, a 'typical' element means an element left unreplaced in the typical body from which a compound is formed.

Dibasic acid hydrogen salts, such as the oxalate, sulphate, &c., form not only salts containing two atoms of ethyle in one molecule of the salt, but they also form double salts containing one atom of ethyle and one atom of hydrogen in each molecule of the salt. Thus we have ethylic oxalate $(C^2\,H_5)_2\,C^2\,O_4$, and hydr-ethylic oxalate $H(C^2\,H_5)\,C^2\,O_4$. So also ethylic sulphate $(C^2\,H_5)_2\,S\,O_4$, and hydr-ethylic sulphate $H\,(C^2\,H_5)\,S\,O_4$, commonly called sulphovinic acid. In like manner there is an ethylic carbonate $(C^2\,H_5)_2\,C\,O_3$, and a hydr-ethylic carbonate $H\,(C^2\,H_5)\,C\,O_3$, called carbovinic acid.

There are also double phosphates containing ethyle and hydrogen, in proportions corresponding to the sodium and hydrogen in the double phosphates containing those elements. Hydro-di-ethylic phosphate is $H\,(C^2\,H_5)_2\,P\,O_4$, di-hydro-ethylic phosphate is $H_2\,(C^2\,H_5)\,P\,O_4$, and the ethylic phosphate, commonly called phosphoric ether, is $(C^2\,H_5)_3\,P\,O_4$.

CHAPTER XXXVI.

239. Vinic Chloride ($Cl\,C^2H_5$ = 2 vols.; boiling-point 11°C.; sp. gr. at 5°C = 0.874) is formed by the action of hydric chloride on vinic alcohol—

$$H\,O\,C^2H_5 + H\,Cl = Cl\,C^2H_5 + H_2O.$$

Also by the action of phosphoric chloride upon the alcohol—

$$H\,O\,C^2H_5 + P\,Cl_5 = Cl\,C^2H_5 + H\,Cl + PO\,Cl_3.$$

It is a colourless liquid, having an agreeable odour, and burns with a bright flame, the borders of which are tinged with green. It is slightly soluble in water.

Vinic Bromide ($Br\,C^2H_5$ = 2 vols.; boiling-point, 41°; sp. gr. 1.4) is analogous to the chloride, and is prepared by similar processes. It is more easily decomposed than the chloride.

Vinic Iodide ($I\,C^2H_5$ = 2 vols.; boiling-point 72°; sp. gr. 1.92) is perfectly analogous to the bromide and chloride, but differs from them in the same way as hydric iodide differs from the bromide and chloride. It is more easily decomposed than the bromide or chloride, and on that account is more serviceable as affording a means of replacing hydrogen or metals by the alcohol radicals. It is obtained by the action of a mixture of iodine and phosphorous iodide on alcohol. It is decomposed by sunlight, a mixture of the three hydrocarbons, C^2H_4, C^2H_6, and C^4H_{10}, being given off, while iodine remains dissolved by the liquid.

Side by side with these ethers should be studied **Vinic Cyanide** which has been prepared by two distinct processes :—

1°. By double decomposition between potassic sulphovinate and potassic cyanide—

$$(C^2H_5)KSO_4 + NCK = K_2SO_4 + NCC^2H_5,$$

or by the action of potassic cyanide upon an alcoholic solution of vinic iodide—

$$IC^2H_5 + NCK = NCC^2H_5 + IK.$$

2°. By the action of phosphoric acid (P_2O_5) on ammonic propionate, the elements of water being abstracted from the salt, and vinic cyanide formed—

$$C^3H_5O_2NH_4 - 2H_2O = NCC^2H_5.$$

The molecule of vinic cyanide occupies two volumes in the state of vapour. By the action of a boiling solution of caustic potash, vinic cyanide is decomposed, ammonia being liberated and potassic propionate formed—

$$NCC^2H_5 + KOH + H_2O = NH_3 + C^3H_5O_2K.$$

Vinic cyanide boils at 88°C.

240. A body of the same composition as this cyanide was prepared by Hofmann, by the action of caustic potash and chloroform on ethylia (C^2H_7N)—

$$C^2H_7N + CHCl_3 + 3KOH = C^2H_5NC + 3KCl + 3H_2O.$$

It is however only slightly attacked by caustic potash, but acid hydrogen salts exert a violent action, hydric formiate and hydrochlorate of ethylia being produced—

$$CNC^2H_5 + 2H_2O + HCl = HCO.OH + ClH_3NC^2H_5.$$

A comparison of this reaction with the action of potash on the first described cyanide, will shew the nature of the isomerism in the two bodies. In the first case the atom of nitrogen goes off as ammonia, while the ethyle group combines with the carbon, the result being the formation of a propionate.

The arrangement thus indicated is $\begin{matrix}N\,C\,C\,C\,H_3\\ \quad\quad H_2\end{matrix}$, and the action of potash consists in the replacement of nitrogen by an atom of divalent oxygen, and an atom of hydroxyl (OH), $\begin{matrix}HO\,C\;\;C\,H_3\\ \quad O\,|\,H_2\end{matrix}$.

The nitrogen combines with three atoms of hydrogen in place of the three combining powers of carbon by which it was previously saturated. In the second case hydrochlorate of ethylia and hydric formiate are produced, the arrangement being $\begin{matrix}C\,N\,C\,C\,H_3\\ \quad\quad H_2\end{matrix}$, and when this breaks up, the terminal atom of carbon is replaced by three atoms of hydrogen and one atom of chlorine, $\begin{matrix}H_3\,N\;\;C\,C\,H_3\\ Cl\,|\,H_2\end{matrix}$, while the carbon combines with an atom of oxygen, one of hydrogen, and one of hydroxyl, $\begin{matrix}H\,C\,O\,H\\ \quad O\end{matrix}$.

241. Vinic Cyanate ($OCNC^2H_5 = 2$ vols.; boiling-point, 60°C) is formed by heating an intimate mixture of potassic cyanate and sulphovinate—

$$OCNK + K(C^2H_5)SO_4 = OCNC^2H_5 + K_2SO_4.$$

It is a liquid of an exceedingly pungent odour. Ethylic cyanurate is formed at the same time and crystallizes out from the cyanate. Its composition corresponds to that of the metallic cyanurates, being $(C^2H_5)_3C_3N_3O_3$.

When vinic cyanate is boiled with caustic potash a decomposition occurs, potassic carbonate, and a kind of ammonia containing an atom of ethyle and two atoms of hydrogen united with an atom of nitrogen, being formed—

$$OCNC^2H_5 + 2KOH = H_2NC^2H_5 + K_2CO_3.$$

This remarkable base was called ethylamine by Würtz, its discoverer, but is now more commonly called ethylia. It was one of the first discovered members of an immense

family of ammonias containing organic radicals in the place of some of the hydrogen of common ammonia.

Ethylic cyanate combines with ammonia, forming a compound called ethyl-urea, being a molecule of urea in which an atom of hydrogen is replaced by ethyle—

$$O\,C\,N\,C^2H_5 + N\,H_3 = H_2\,N\,\underset{O}{C}\,N\,(C^2H_5)\,H.$$

Common urea is $H_2\,N\,\underset{O}{C}\,N\,H_2$.

A body isomeric with this cyanate was formed by the action of chloride of cyanogen upon sodic ethylate—

$$Na\,O\,C^2H_5 + N\,C\,Cl = N\,C\,O\,C^2H_5 + Na\,Cl.$$

By the action of potash, alcohol and potassic cyanurate are formed. This reaction shews that this body corresponds to a normal ether, the potassium simply taking the place of the ethyle—

$$N\,C\,O\,C^2H_5 + K\,O\,H = N\,C\,O\,K + H\,O\,C^2H_5.$$

Ethylic Sulphocyanate ($N\,C\,S\,C^2H_5$ = 2 vols.) is obtained by distilling a mixture of potassic sulphocyanate and potassic sulphovinate in concentrated aqueous solution—

$$N\,C\,S\,K + K\,(C^2H_5)\,S\,O_4 = N\,C\,S\,C^2H_5 + K_2\,S\,O_4.$$

It sinks to the bottom of water, and boils at 146°. By the action of potassic hydrate it has not been found to yield ethylia.

242. There are ethers corresponding to monovalent nitrites and nitrates. By the action of hydric nitrate on alcohol a mixture of products of oxidation of the alcohol with a nitrite is usually obtained, and for the preparation of the pure nitrites it is found most advantageous to mix the alcohol with hydric nitrate in the cold, and to add copper turnings to the mixture.

Vinic Nitrite ($C^2H_5NO_2$ = 2 vols.), or nitrous ether, should be made to pass from the flask in which it is generated, through a bottle of water, and then through

a tube full of calcic chloride. It condenses to a liquid which boils at about 21°, and has an exceedingly fragrant agreeable odour.

It was discovered by Millon that the presence of urea in a mixture of alcohol and hydric nitrate prevents the oxidizing action which otherwise takes place upon the alcohol, and consequently prevents the formation of a nitrite.

Ethylic Nitrate ($C^2H_5NO_3$), obtained in this manner, is a liquid heavier than water and quite insoluble in it. It boils at 85°, and its vapour explodes with violence when much heated.

243. The compounds which ethyle forms with dibasic acids must next be studied. The oxalates and carbonates are of two classes, viz. normal salts, such as vinic oxalate $C^2O_2(OC^2H_5)_2$, which contain two atoms of ethyle in each molecule while occupying the normal molecular volume. There are also double oxalates, such as hydro-vinic oxalate $C^2O_2(OH)(OC^2H_5)$, and vino-potassic oxalate $C^2O_2(OK)(OC^2H_5)$.

Vinic Oxalate ($C^2O_2(OC^2H_5)_2 = 2$ vols.; boiling-point, 182°; sp. gr. 1.1) is formed by passing gaseous hydric chloride into a mixture of dry alcohol and hydric oxalate, or by heating the mixture with hydric sulphate. In either case the acid salt accelerates a process which takes place more slowly without its intervention. The ether is almost insoluble in water. Its solution in alcohol is decomposed by the cautious addition of potash, with formation of a precipitate of vino-potassic oxalate, whilst alcohol is formed.

Ammonia decomposes the ether rapidly, with formation of oxamide and alcohol—

$$C^2O_2(OC^2H_5)_2 + 2NH_3 = C^2O_2(NH_2)_2 + 2(HOC^2H_5).$$

By the cautious addition of an alcoholic solution of ammonia to a similar solution of the ether, an intermediate

compound is formed, consisting of crystalline plates possessing the composition—

$$C^2O_2(OC^2H_5)_2 + NH_3 = C^2O_2(NH_2)(OC^2H_5) + HOC^2H_5.$$

This compound is considered as an oxamate. No monobasic ether could be decomposed in two steps as this is, an intermediate product being found consisting of half oxalic ether, and half oxamide. Oxalic ether is gradually decomposed by cold water, but more rapidly by boiling water, the ultimate products being alcohol and hydric oxalate. The formation and subsequent decomposition of this ether afford the best means of obtaining hydric oxalate free from mineral impurity, as the ether is easily purified by distillation.

244. Vinic Carbonate ($CO(OC^2H_5)_2 = 2$ vols.) is most easily obtained by the action of metallic sodium on vinic oxalate.

Strong alcohol, in which potassic hydrate has been dissolved, contains potassic ethylate (KOC^2H_5), and accordingly carbonic acid passed into the liquid forms vino-potassic carbonate by uniting with the ethylate. A good deal of potassic carbonate is formed at the same time, but being insoluble in alcohol, this salt goes down, whilst the double salt remains in part at least in the liquid, from which it can be precipitated by the addition of ether. The formation of this body is represented by the equation—

$$KOC^2H_5 + CO_2 = CO(OK)(OC^2H_5).$$

The sulphur salts corresponding to these carbonates are easily obtained by corresponding processes. Thus vinic sulpho-carbonate, $CS(SC^2H_5)_2$, is formed by the action of vinic chloride on the double salt $CS(SK)(SC^2H_5)$, and this double salt is obtained by pouring carbonic sulphide into an alcoholic solution of potassic sulphide, which no doubt contains ethyl-potassic sulphide (KSC^2H_5).

245. Sulphurous acid forms a normal ethyle salt, which is obtainable by the action of hyposulphurous chloride on

absolute alcohol. It is a colourless liquid, somewhat heavier than water, and nearly insoluble in it. Its molecule occupies the normal volume, and contains two atoms of ethyle—

($S\,O\,(O\,C^2\,H_5)_2$ = 2 vols.; boiling-point, 160°).

Hydro-vinic Sulphite ($S\,O\,(O\,H)\,(O\,C^2\,H_5)$) is formed by the action of hydric nitrate on mercaptan. It can be obtained in crystals from a concentrated aqueous solution. Its salts, even with barium and lead, are soluble in water.

Vinic Sulphate ($S\,O_2\,(O\,C^2\,H_5)_2$) is formed by passing the vapour of sulphuric acid into ether cooled by immersion in a freezing mixture. The product is shaken up with a mixture of ether and water, the sulphate being dissolved by the former, while various foreign bodies are dissolved by the water. The sulphate is obtained by evaporation of its ethereal solution. It cannot be distilled without decomposition.

246. Far more important are the double sulphates containing ethyle and metals, the so-called sulphovinates. Sulphovinic acid is formed simultaneously with water by mixing alcohol and hydric sulphate—

$$H\,O\,C^2\,H_5 + S\,O_2\,(O\,H)_2 = S\,O_2\,(O\,H)\,(O\,C^2\,H_5) + H_2\,O.$$

The mixture after standing for some days, or after heating, should be poured in a fine stream into an excess of slaked lime suspended in water with lumps of ice, and the mass should be constantly agitated while the acid mixture flows into it. Calcic sulphate and sulphovinate are formed, and the latter, being readily soluble in water, is separated by filtration, and crystallized from its solution by evaporation.

The salt crystallizes in plates which contain two molecules of water of crystallization—

$$Ca\,(C^2\,H_5)_2\,(S\,O_4)_2\,(H_2\,O)_2.$$

The solution of this or of any neutral sulphovinate can be heated in presence of water without undergoing decompo-

sition; but when the basic metal is replaced by hydrogen, by the addition of hydric chloride or sulphate, the double sulphate decomposes easily, alcohol and a sulphate being formed. Thus an aqueous solution of baric sulphovinate deposits baric sulphate when boiled with hydric chloride—

I. $Ba(C^2H_5)_2(SO_4)_2 + 2HCl = 2H.C^2H_5SO_4 + BaCl_2$;

II. $H.C^2H_5SO_4 + H_2O = H_2SO_4 + HOC^2H_5$;

III. $H^2SO_4 + BaCl_2 = BaSO_4 + 2HCl$.

When a mixture of sulphovinic acid and alcohol is heated, an interchange between ethyle in the former and typical hydrogen in the latter takes place; thus—

$$HC^2H_5SO_4 + HOC^2H_5 = H_5C^2OC^2H_5 + H_2SO_4,$$

ether and hydric sulphate being formed.

Thus the formation of ether from alcohol and hydric sulphate takes place in two stages, the first part being the formation of sulphovinic acid and water, the second, the formation of ether and hydric sulphate by the mutual action of sulphovinic acid and alcohol. The ether thus formed evaporates, and must be collected by a suitable condenser. The sulphate which is reproduced at the end of the process is usually employed for the transformation of more alcohol into ether and water, and for that purpose it is kept at the same temperature of 135°, while alcohol is allowed to flow into it slowly by a tube reaching to the bottom of the vessel containing it. The flow of alcohol should be regulated so as to keep the surface of the mixture in the retort constantly at its initial height.

247. The alcohol which comes into contact with this sulphate reacts in the same manner as that which was first mixed with it—forming water, which distils off, and sulphovinic acid; and this sulphovinic acid in its turn reacts on another molecule of alcohol, forming ether and the original sulphate. Thus it is that a given quantity of sulphate transforms an indefinite quantity of alcohol into these two pro-

ducts. The sulphate is renewed occasionally, because it gets contaminated by impurities in the alcohol, and by secondary products, which impair its action.

The liquid collected in the receiver consists of two strata; the lower one being chiefly water, the upper stratum impure ether. Sulphurous acid is usually present in the distillate, and is removed by washing the ether with caustic soda; alcohol is always carried over with the ether and water, and can be partially removed by washing with salt water, in which it is far more soluble than the ether. To obtain the ether pure it should be finally distilled over powdered sodic hydrate, or even metallic sodium, which keep back any water or alcohol.

248. Ether ($H_5C^2OC^2H_5$ = 2 vols.; boiling-point, 35°; Sp. gr. = 0.736) is an exceedingly mobile liquid. It has an agreeable odour, which is well known under the name 'ethereal.' It produces an anæsthetic effect when inhaled in sufficient quantity, but its use for this purpose has been given up, owing to the unpleasant after-effects which it produces on the patient. It is dissolved by about fourteen times its volume of water; but if there be not water enough to dissolve it, the supernatant stratum of ether takes up about $\frac{1}{36}$ of its volume of water, which it holds in solution. When poured on the hand, ether produces a strong sensation of cold, owing to the rapidity with which it evaporates, heat being rendered latent. Its vapour density is 37, as can be seen from the fact that its molecule $(C^2H_5)_2O$, weighing 74, occupies two volumes in the state of vapour.

Being about $2\frac{1}{2}$ times as heavy as air, ether vapour can easily be poured from one vessel to another. It very easily catches fire, and burns with a white flame. A mixture of ether vapour and air explodes with great violence if containing oxygen in about the combining proportions, viz. six volumes to every one of ether vapour. Ether ought

never to be distilled in the vicinity of fire or flame, but hot water should be brought from a distance to pour into the vessel in which the retort full of ether is contained. Ether dissolves oils, and fats, and resins far more readily than alcohol dissolves them. It also dissolves sulphur, phosphorus, and iodine.

Metallic salts are as a rule less soluble in ether than in alcohol, and many salts which dissolve readily in alcohol can be precipitated from that solution by the addition of ether.

Hydric sulphate dissolves ether readily, doubtless forming alcohol and sulphovinic acid—

$$(C^2H_5)_2O + H_2SO_4 = HOC^2H_5 + H(C^2H_5)SO_4;$$

and probably also water and a second molecule of sulphovinic acid, by the action of hydric sulphate upon the alcohol thus produced.

Sulphuric acid combines with ether as with water, forming vinic sulphate $(C^2H_5)_2SO_4$.

CHAPTER XXXVII.

249. The analogy between oxygen and sulphur, between sulphur and selenium, and between selenium and tellurium, naturally suggests the probability of these elements being able to replace oxygen, atom for atom, in alcohol and ether —forming sulphides, selenides, tellurides, &c. analogous to the oxide and hydrate. As far as experiments have gone as yet, these anticipations have been confirmed.

Mercaptan ($HSC^2H_5 = 2$ vols.; boiling-point, 62°; sp. gr. 0.835) is obtained by distilling a mixture of calcic sulphovinate and hydropotassic sulphide—

$$Ca(C^2H_5)_2(SO_4)_2 + 2HSK = 2HS(C^2H_5) + K_2SO_4 + CaSO_4.$$

It is more easily formed by the action of vinic iodide upon an alcoholic solution of potassic sulph-hydrate—

$$IC^2H_5 + HSK = HSC^2H_5 + KI.$$

Mercaptan floats upon water and is almost insoluble in it. At a low temperature it crystallizes. Hydric nitrate oxidizes it, forming hydro-vinic sulphite ($HC^2H_5SO_3$).

The addition of mercuric oxide precipitates the sulphur alcohol in combination with mercury in the form of the compound ($H_5C^2SHgSC^2H_5$), which is decomposed by sulphuretted hydrogen—

$$H_2S + (C^2H_5)_2HgS_2 = HgS + 2HSC^2H_5.$$

The compound C^2H_6S is called 'mercaptan' from the force with which it reacts upon mercuric oxide. It is remarkable for its peculiarly disagreeable smell.

250. Vinic Sulphide ($H_5C^2SC^2H_5$ = 2 vols.; boiling-point, 73°; sp. gr. 0.825) is prepared by the action of potassic sulphide upon calcic sulphovinate, and also by its action upon vinic iodide. It can be precipitated from its alcoholic solution by the addition of water. It has an odour resembling that of garlic.

There is also a vinic disulphide—

$$H_5C^2SSC^2H_5.$$

These compounds are analogous to alcohol and ether, and they are to be considered as derived from them by the substitution of an atom of sulphur for an atom of oxygen; the resulting sulphur compound occupying the same vapour-volume as the original oxygen compound. Vinic alcohol is decomposed by phosphoric sulphide, forming mercaptan, an atom of sulphur going into the place of the atom of oxygen in the alcohol; whereas when it is decomposed by phosphoric chloride, the atom of oxygen being replaced by two atoms of chlorine, the result is the formation of a molecule of vinic chloride plus a molecule of hydric chloride—

$$HOC^2H_5 + PCl_5 = OPCl_3 + ClC^2H_5 + HCl.$$

If sulphur were monovalent, like chlorine, the phosphoric sulphide would form vinic sulphide and hydric sulphide in separate molecules instead of the compound $HS(C^2H_5)$.

251. Side by side with these bodies, containing divalent elements, may be considered compounds of the dyads zinc and mercury with ethyle. These compounds are of two classes; one class consisting of compounds of one atom of metal with two atoms of ethyle, such as $Zn(C^2H_5)_2$, $Hg(C^2H_5)_2$, &c.; the other class consisting of compounds of one atom of metal and one atom of chlorine or iodine, &c., such as $IZnC^2H_5$, $IHgC^2H_5$, &c. The latter class must be considered as double salts in which the ethyle has chlorous functions. The compounds belonging to it may be compared to the inorganic salts of the corresponding

metals, such as $Zn Cl_2$, $Hg I_2$, &c., one atom of the chlorous constituent of these being replaced by an atom of ethyle. They are formed by the action of the metals upon the corresponding ether. Thus zinc combines with vinic iodide, forming **zinc-eth-iodide** (Et Zn I).

The best way to obtain the compound is to use zinc amalgam, containing 12 to 15 per cent. of mercury, and in the state of fine powder. In a glass bottle the combination is complete after contact of two or three weeks at the ordinary temperature, when enough amalgam is used to fill the liquid; but it is complete in a few hours if the same mixture be heated to 100° in an iron digester.

The compound consists of scaly crystals, which are easily decomposed by distillation, even in vacuo, the products being zinc ethide, which distils over, and zinc iodide which remains behind—

$$2\,I\,Zn\,C^2\,H_5 = H_5\,C^2\,Zn\,C^2\,H_5 + Zn\,I_2.$$

Zinc ethide is a liquid heavier than water. It catches fire spontaneously in contact with air, but when oxygen is brought gradually into contact with the ethide, zinc alcohol is formed, Et O Zn O Et; where the symbol Et is used to represent the radical ethyle, $C^2 H_5$.

Zinc ethide occupies two volumes in the state of vapour, the two atoms of ethyle being held together by one atom of zinc. It boils at 110°C. Ammonia gas decomposes it, zinc amide and ethylic hydride being formed—

$$Zn\,(C^2\,H_5)_2 + 2\,N\,H_3 = Zn\,(N\,H_2)_2 + 2\,C^2\,H_6.$$

Potassium decomposes zinc ethide, forming a solution of potassic ethide in the zinc compound—

$$Zn\,(C^2\,H_5)_2 + K^2 = 2\,K\,C^2\,H_5 + Zn.$$

By the action of carbonic acid on potassic ethide Wanklyn obtained potassic propionate—

$$K\,C^2\,H_5 + C\,O_2 = K\,O\,C\,C^2\,H_5.$$
$$\qquad\qquad\qquad

By heating zinc ethide with ethylic iodide, Frankland obtained the so-called 'ethyle' or ethylic ethide—

$$Zn\,(C^2\,H_5)_2 + 2\,I\,C^2\,H_5 = Zn\,I_2 + 2\,H_5\,C^2\,C^2\,H_5.$$

The gas $H_5\,C^2\,C^2\,H_5$ or $C^4\,H_{10}$ thus formed, yielded by the action of chlorine a liquid of the composition $C^4\,H_9\,Cl$, which behaved like the chloride of a radical $C^4\,H_9$, differing from ethyle by the increment $2\,C\,H_2$. This reaction was not expected upon the view that 'ethyle' had a different constitution from the hydride of the radical butyle $C^4\,H_9$.

At a pressure of 2.5 atmospheres ethyle ($C^4\,H_{10}$) condenses to a liquid at 3°C, and at the ordinary atmospheric pressure it requires a temperature of −23°C for its liquifaction.

252. Mercuric Eth-iodide ($I\,Hg\,C^2\,H_5$) is most easily obtained by combination of mercuric iodide with mercuric ethide—

$$Hg\,I_2 + Hg\,(C^2\,H_5)_2 = 2\,Hg\,(I\,C^2\,H_5).$$

Mercuric Ethide ($H_5\,C^2\,Hg\,C^2\,H_5$) is easily obtained by Frankland and Duppa's process of acting on ethylic iodide in presence of a little acetic ether by very weak sodium amalgam. It is a heavy, colourless liquid, boiling at 159°C. Its formula $Hg\,(C^2\,H_5)_2$ corresponds to two volumes of vapour. Its density is 2.46.

Mercuric ethide is not decomposed by alcoholic potash. Hydric bromide decomposes it, evolving ethylic hydride and forming mercuric eth-bromide—

$$Hg\,(C^2\,H_5)_2 + H\,Br = Br\,Hg\,C^2\,H_5 + C^2\,H_6.$$

Bromine forms ethylic bromide, and the ethylo-bromide—

$$Hg\,(C^2\,H_5)_2 + Br^2 = Br\,Hg\,C^2\,H_5 + Br\,C^2\,H_5.$$

Neither compound is decomposed by water, but both are decomposed by metallic zinc, and by metallic aluminium.

253. The compounds formed by ethyle with trivalent salt

radicals correspond in their mode of formation and in their general properties to the other salts. Thus, there are the three phosphates—

$$(C^2H_5)_3PO_4;\ H(C^2H_5)_2PO_4;\ H_2(C^2H_5)PO_4.$$

The typical hydrogen in the last two is replaceable by basylous metals, forming salts, such as the di-ethyl-sodic phosphate $(C^2H_5)_2NaPO_4$, &c. There are also similar phosphites, such as ethylic phosphite $(C^2H_5)_3PO_3$, &c. Thus vinic phosphite is obtained by the action of phosphorous chloride on sodic ethylate—

$$PCl_3 + 3\,NaOC^2H_5 = 3\,NaCl + PO_3(C^2H_5)_3.$$

It is thus formed from three molecules of alcohol, which are held together by the triad phosphorus replacing one atom of hydrogen in each molecule. Vinic phosphate may similarly be represented as containing the trivalent radical PO in the place of three atoms of hydrogen from three molecules of alcohol; $PO(OC^2H_5)_3$.

Vinic Borate ($(C^2H_5)_3BO_3$ = 2 vols.; boiling-point, 119°) is formed by the action of boric chloride on alcohol—

$$BCl_3 + 3\,HOC^2H_5 = 3\,ClH + BO_3(C^2H_5)_3.$$

Zinc ethide desoxidizes this ether completely, forming boric ethide, $B(C^2H_5)_3$.

By the action of chloroform on sodic ethylate a compound has been obtained, consisting of three molecules of alcohol in which the three atoms of typical hydrogen are replaced by the group (CH), viz. $(CH)O_3(C^2H_5)_3$. By the action of hydric chloride it is decomposed, forming ethylic formiate, $(CHO)OC^2H_5$, and ether, $O(C^2H_5)_2$.

254. Amongst the most remarkable of compounds containing ethyle are the bases analogous to ammonia, but containing ethyle in the place of one or more atoms of hydrogen of ammonia.

Ethylia (C^2H_7N) can be prepared by the action of am-

monia on ethylic bromide. A direct combination takes place when the substances are heated together under pressure, forming ethyl-ammonic bromide ($N H_3 (C^2 H_5) Br$); and when this salt is distilled with caustic potash, ethylia goes over.

Ethylia can be condensed to a liquid which boils at 18.7°C. Its density at 8° was found to be 0.696. In the state of vapour its molecule occupies two volumes ($C^2 H_7 N$ = 2 vols.). Its vapour density is therefore 22.5.

It combines with acid hydrogen salts in the same manner as ammonia combines with them, forming compounds such as $N H_3 (C^2 H_5) Cl$, $(N C^2 H_8)_2 S O_4$, &c. It precipitates the heavy metallic oxides from solutions of their salts, and dissolves cupric oxide. It differs from ammonia by dissolving alumina, when added in excess to a solution of a salt of that base. Its hydro-chlorate combines with platinic chloride in the same proportion as ammonic chloride combines with it; but the double chloride $Pt Cl_6 N_2 (C^2 H_5)_2 H_6$ is more soluble in water than the compound formed from ammonia.

255. Di-ethylia ($(C^2 H_5)_2 H N$ = 2 vols.; boiling-point, 57°C) can be obtained from ethylia by the action of ethylic bromide, and subsequent distillation with potash. It resembles ethylia very much in its reactions, but when the two bases are mixed with one another they can be separated by the action of oxalic ether, which forms with di-ethylia a compound called di-ethyl-oxamic ether, which is insoluble in water; whereas ethylia forms under these circumstances di-ethyl-oxamide, a crystalline body which is dissolved by water. Both of these compounds are decomposed by boiling potash; the one yielding ethylia, the other di-ethylia. This beautiful reaction was discovered by Hofmann.

Tri-ethylia ($(C^2 H_5)_3 N$ = 2 vols.; boiling-point, 91°C) is formed from di-ethylia by the further action of ethylic bro-

mide. Tri-ethylia combines in its turn with ethylic bromide, or still better with ethylic iodide—

$$N(C^2H_5)_3 + I\,C^2H_5 = N(C^2H_5)_4\,I.$$

The salt thus formed contains **Tetr-ethyl-ammonium**, $N(C^2H_5)_4$, and other salts can be prepared from it by processes of double decomposition. Thus a solution of the iodide shaken up with freshly-precipitated argentic hydrate, forms argentic iodide and tetr-ethyl-ammonic hydrate—

$$N(C^2H_5)_4\,I + Ag\,O\,H = N(C^2H_5)_4\,O\,H + Ag\,I.$$

This remarkable base is best described by comparison with potash, which it resembles in its strongly caustic properties. It is decomposed by distillation, yielding tri-ethylia, ethylene, and water—

$$N(C^2H_5)_4\,O\,H = N(C^2H_5)_3 + C^2H_4 + H_2O.$$

When ammonia is heated with ethylic iodide a mixture is obtained of the five salts, NH_4I, NC^2H_8I, $N(C^2H_5)_2H_2I$, $N(C^2H_5)_3HI$, and $N(C^2H_5)_4I$. By distilling the mixture with potash, a distillate is obtained containing ammonia, ethylia, di-ethylia, and tri-ethylia. The last three are separated by the action of oxalic ether, for tri-ethylia does not react on the ether, and can be distilled off by the heat of the water-bath, together with the alcohol formed in the reaction, from the di-ethyl-oxamide and di-ethyl-oxamic ether. On the separation of these two by water, as above described, the di-ethyl-oxamic ether is accompanied by oxamide, but the ammonia evolved by the decomposition of the oxamide can easily be separated from the di-ethylia.

256. Similar bases to these have been prepared with phosphorus instead of nitrogen. Zinc ethide combines with phosphorous chloride, and the compound

$$3\,Zn(C^2H_5)_2 + 2\,P\,Cl_3 = (Zn\,Cl_2)_3\,(P(C_2H_5)_3)_2$$

yields on distillation with caustic potash a base containing in each molecule one atom of phosphorus combined with three atoms of ethyle ($P(C^2H_5)_3$ = 2 vols.). This body catches

fire spontaneously in the air. It combines rapidly with vinic iodide, forming iodide of phosphorus ammonium. It is insoluble in water, and has a density of 0.812. It boils at 127°. It combines with oxygen, sulphur, iodine, &c., forming bodies such as

$$P(C^2H_5)_3O,\ P(C^2H_5)_3S,\ P(C^2H_5)I_2,\ \&c.$$

There seems to be another compound of phosphorus with ethyle of the composition $P^2(C^2H_5)_4$.

257. Arsenic forms a series of compounds with ethyle which are very important. By the action of vinic iodide on sodic arsenide a compound is formed, called ethyle-kakodyle, having the composition represented by the formula $As^2(C^2H_5)_4$. It unites directly with chlorine—

$$2\ As(C^2H_5)_2 + Cl^2 = 2\ As(C^2H_5)_2Cl.$$

$As(C^2H_5)_2$ is thus a monovalent radical combining with chlorine in the same manner as the radical ethyle combines with it. In the free state two atoms of this radical unite, thus—

$$(H_5C^2)_2As\,As(C^2H_5)_2.$$

It absorbs oxygen rapidly, catching fire spontaneously on contact with the air.

Another compound of arsenic and ethyle is tri-ethyl-arsine, $As(C^2H_5)_3$, corresponding in its constitution to triethylia. It is the chief product obtained by the action of vinic iodide upon sodic arsenide, the compound previously mentioned being another product. It boils at 140°C. It combines with chlorine, and with oxygen, forming the compounds $As(C^2H_5)_3Cl_2$, $As(C^2H_5)_3O$, in which the arsenic is pentavalent. It unites directly with vinic iodide, producing the iodide of tetr-ethyl-arsonium, $As(C^2H_5)_4I$.

The various compounds containing arsenic in combination with ethyle salt radicals are best arranged in the types $AsCl_3$ and $As(C^2H_5)_4Cl$, the arsenic being trivalent in the one class of compounds and pentavalent in the other.

The first may be called the ammonia type, the second the ammonic-chloride type. In the former type are the compounds—

$As Et_2 Cl$	$As Et_2 H O$	$As Et I_2$
$As Et_2 Br$	$As Et Cl_2$	$As Et O$
$As Et_2 I$	$As Et Br_2$	$As Et S$.
$As Et_2 CN$	$As Et I_2$	

In the ammonic-chloride type are such compounds as—

$As Et_4 Cl$	$As Et_3 I_2$	$As Et Cl_4$
$As Et_4 Br$	$As Et_3 O$	$As Et_4 As$
$As Et_4 I$	$As Et_3 S$	$As Et_4 O H$.
$As Et_3 Br_2$	$As Et_2 Cl_3$	

258. Antimony also combines with ethyle, forming stib-ethyle, $Sb Et_3$. It is obtained by the action of sodic stibide on vinic iodide. It is also obtained by the action of antimonious chloride on zinc-ethide. It combines with oxygen, forming a compound on the ammonic-chloride type $Sb Et_3 O$. It is even said that stib-ethyle decomposes hydric chloride with evolution of hydrogen—

$$Sb Et_3 + 2 H Cl = Sb Et_3 Cl_2 + H_2.$$

Bismuth also forms compounds with ethyle in the ammonia type, such as $Bi Et_3$ and $Bi Et Cl_2$, but they are not volatile without decomposition.

Aluminic ethide ($Al^2 Et_6$ = 2 vols.) has been formed by the action of aluminium on mercuric ethide. At temperatures moderately above its boiling-point it was found to occupy the normal volume, but at a higher temperature it yielded nearly four volumes.

259. With tetravalent salt radicals ethyle forms salts, of which each molecule contains four atoms of ethyle. Thus argentic pyrophosphate $Ag_4 P_2 O_7$ is decomposed by ethylic iodide, forming $Et_4 P_2 O_7$.

Silicic chloride, by acting on absolute alcohol, forms an ether containing one atom of silicon in the place of the four

atoms of typical hydrogen of four molecules of alcohol $Si O_4 Et_4$. This remarkable body is insoluble in water, but is gradually decomposed by contact with it into gelatinous silica and alcohol. It boils without decomposition at 165°, and its vapour has the density of 146°, corresponding to $C_8 H_{20} Si O_4 = 2$ vols. Another silicic ether, containing only two atoms of ethyle in each molecule, has been described—

$$Et_2 Si O_3 : \text{boiling-point, } 360°.$$

A hexatomic compound, $Si_2 Et_6 O_7$, intermediate between the last two, has also been described.

This hex-ethylic di-silicate is formed by the removal of the elements of a molecule of ether from two molecules of the normal silicate—

$$2\,Et_4 Si O_4 - Et_2 O = Et_6 Si_2 O_7,$$

just as the so-called pyrophosphate is formed from two molecules of hydro-di-sodic phosphate by the removal of a molecule of water—

$$2\,H Na_2 P O_4 - H_2 O = Na_4 P_2 O_7.$$

Silicic ethide ($Si Et_4 = 2$ vols.) has been obtained by the action of zinc ethide on silicic chloride. The compound is lighter than water, and boils without decomposition between 152° and 154°. It is not attacked either by hydric nitrate or by potash.

260. Tin forms with ethyle a variety of compounds belonging to the type of marsh gas. They are obtained by the action of sodic stannide on ethylic iodide. When the stannide is rich in sodium the tin combines with four atoms of ethyle, but when a less energetic alloy is used, one or more atoms of iodine remain in combination with tin instead of one or more atoms of ethyle. Thus there are the following compounds—stannic ethide ($Sn Et_4 = 2$ vols.); stannic tri-ethyl iodide ($Sn Et_3 I$), and chloride, &c.; stannic di-ethyl iodide ($Sn Et_2 I_2$), or nitrate $Sn Et_2 (N O_3)_2$.

Plumbic Ethide ($Pb Et_4$) is obtained by the action of

plumbic chloride on zinc ethide. The mixture becomes black from the liberation of finely-divided metallic lead; and on distilling it at a reduced pressure, a compound of lead with four atoms of ethyle is separated out from it. It boils at about 200°C. The existence of this compound proves that the atomic value of lead is four. All the compounds of lead known in mineral chemistry can be represented on the supposition that the metal is divalent, but in this compound, at least, it must be tetravalent. In the compound of lead with two atoms of oxygen, it may be tetravalent, but it is possible to represent the two atoms of oxygen to be combined with one another to the extent of half their combining power $Pb\begin{matrix}O\\O\end{matrix}$, in which case the lead would be divalent.

By the action of hydric chloride on plumbic ethide a plumbic tri-etho-chloride is obtained, with evolution of ethylic hydride—

$$Pb\,(C^2H_5)_4 + H\,Cl = Pb\,(C^2H_5)_3\,Cl + C^2H_6.$$

A plumb-ethylic sulphate corresponding to this chloride has been obtained. Its formula is $(Pb\,Et_3)_2\,S\,O_4$.

CHAPTER XXXVIII.

261. Methylic Alcohol, or wood-spirits (CH_4O = 2 vols.; density at 0.82°; boiling point, 66°). This substance is formed, together with a variety of other liquid compounds and several gases, by the destructive distillation of wood. A considerable quantity of tar is deposited from the products which pass off from the retort in which the wood is distilled, and with this tar is water containing hydric acetate and wood-spirits. This watery liquid is usually neutralized by lime, and distilled. The crude wood-spirit comes over in the beginning of the distillation accompanied by a little water, and it is usually introduced into commerce, after partial drying by distillation over quicklime. In this state it is usually a yellowish liquid, of an unpleasant smell. It is often called 'naphtha,' or 'wood-naphtha.' Its chief use is for mixing with spirits of wine to form the so-called methylated spirit, which manufacturers are allowed to use without paying the excise duty which is levied on other spirits of wine.

Methylated spirit contains 10 per cent. of wood-spirit, and possesses the characteristic smell of that mixture.

262. Common **Wood-spirit** generally becomes turbid when mixed with water, owing to the precipitation of liquid hydrocarbons which were dissolved in it.

For the preparation of methylic alcohol it should be mixed with nearly its own volume of strong caustic soda-solution, and allowed to stand in a closed vessel for several

hours. The liquid which in most cases collects on the surface should be removed from the alkaline mixture, and the latter distilled as long as any combustible distillate comes over. The sodic solution which is left behind contains a large quantity of sodic acetate, which was formed simultaneously with methylic alcohol by the action of the soda on methylic acetate contained in the crude wood-spirit. This distillate usually contains ammonia, and should be distilled with 3 or 4 per cent. of hydric sulphate, which not only keeps back the volatile bases but also a good deal of tarry matter formed from impurities in the wood-spirit. In this manner a mixture of methylic alcohol with water, acetone, and di-methylacetal is obtained; and to get rid of the two last-named bodies, the mixture should be saturated with dry calcic chloride, and distilled in a water-bath as long as anything comes over at that temperature. The distillate consists of acetone, di-methylacetal, and sometimes a part of the methylic alcohol; and the calcic chloride in the retort retains methylic alcohol in the form of a compound which is not decomposed at the temperature of 100°. In order to liberate the alcohol from this compound, water should be added in small quantity and the mixture should then be distilled. The alcohol which comes over requires subsequent drying by means similar to those described for drying common vinic alcohol.

When required in the purest obtainable state methylic alcohol is made by the action of ammonia on methylic oxalate—

$$(CH_3)_2C^2O_4 + 2NH_3 = 2CH_4O + N_2H_4C^2O_2;$$

oxamide being formed at the same time.

The filtered liquid is neutralized by hydric sulphate, to take up the excess of ammonia, and distilled. The distillate consists of a mixture of water and pure **Methylic Alcohol.**

263. This remarkable liquid has great resemblance to vinic alcohol in its properties. It mixes with water in all proportions, and with condensation.

Potassium or sodium dissolves in it with evolution of hydrogen, forming solutions of the compounds $K C H_3 O$ or $Na C H_3 O$, called respectively potassic methylate and sodic methylate. Methylic alcohol dissolves caustic potash or soda, forming these same compounds together with water—

$$H C H_3 O + K H O = K C H_3 O + H H O.$$

Monobasic hydrogen salts, such as the chloride, iodide, nitrate, &c., react upon methylic alcohol in like manner as upon vinic alcohol, forming water and compounds of methyle, such as methylic chloride ($C H_3 Cl$), iodide ($C H_3 I$), or nitrate ($C H_3 N O_3$). In these reactions the radical methyle changes places with an atom of hydrogen, just as an atom of ethyle does in the corresponding reactions of these salts on vinic alcohol, and a molecule of water is formed in each case from a molecule of methylic alcohol, by the replacement of its methyle by hydrogen, the vapour-volume being unaltered by the interchange—

$$\overset{2\text{ vols.}}{H (C H_3) O} + \overset{2\text{ vols.}}{H Cl} = \overset{2\text{ vols.}}{H H O} + \overset{2\text{ vols.}}{(C H_3) Cl}.$$

Dibasic acids form both normal salts with methyle, such as

$(C H_3)_2 C^2 O_4$, methylic oxalate;
$(C H_3)_2 S O_4$, methylic sulphate;
$(C H_3)_2 C O_3$, methylic carbonate:

and also double salts, such as

$H C H_3 C^2 O_4$, hydro-methylic oxalate or oxalo-methylic acid;
$H C H_3 S O_4$, hydro-methylic sulphate or sulpho-methylic acid;
$H C H_3 C O_3$, hydro-methylic carbonate or carbo-methylic acid.

Tribasic acid salts, such as hydric phosphate, form not only normal methyle salts, containing three atoms of methyle in each molecule of the salt, such as methylic phos-

phate $(C H_3)_3 P O_4$; they also form two classes of double salts: one, in which one-third of the methyle is replaced by hydrogen or a metal, such as the hydro-di-methylic phosphate $H (C H_3)_2 P O_4$; another, in which two-thirds of the methyle are so replaced, as in the case of the di-hydro-methylic phosphate $H_2 C H_3 P O_4$.

Hydric sulphate when heated with one-quarter its weight of methylic alcohol decomposes it into so-called methylic ether ($C^2 H_6 O$) and water—

$$2 H C H_3 O = C^2 H_6 O + H H O.$$

Carbonic acid, sulphurous acid, and other products are formed at the same time. All attempts to form from methylic alcohol the hydrocarbon $C H_2$, as olefiant gas is formed from vinic alcohol, have failed.

264. Methylic alcohol is admitted to be constituted like vinic alcohol, having the radical methyle ($C H_3$) in the place of the ethyle ($C^2 H_5$) of vinic alcohol; and similar arguments to those which served to establish that vinic alcohol is a molecule of water ($H H O$) in which one atom of hydrogen is replaced by an atom of ethyle ($(C^2 H_5) H O$) may be used to prove that methylic alcohol is formed from water by the replacement of one atom of hydrogen by methyle ($(C H_3) H O$).

The two alcohols differ empirically in composition by the elements $C H_2$; for if these elements were taken from vinic alcohol without disarranging the remaining elements, methylic alcohol would be formed ($C^2 H_6 O - C H_2 = C H_4 O$).

The term '**homologous**' is applied to bodies possessing analogous properties, as shewn by their reactions, and differing from one another by $C H_2$, or any multiple of $C H_2$. It was stated above that the action of the sulphate upon methylic alcohol gives rise to the formation of a product having a composition represented by the empirical formula $C^2 H_6 O$.

The density of this compound in the state of vapour is identical with that of alcohol vapour—

$$C^2 H_6 O = 2 \text{ vols.};$$

but this methylic ether is a vapour at the common atmospheric temperature, and when condensed to the liquid state is found to have the boiling-point $-23.5°C$, whilst vinic alcohol boils at 78°.

The study of the reactions of methylic ether shews that its constitution is not analogous to that of methylic alcohol, so that it is not homologous with it. For each molecule of methylic ether ($(C H_3)_2 O$) is found to contain two atoms of methyle, of which one or both can be removed and replaced by hydrogen, atom for atom; and in no reactions does it shew a behaviour like alcohol, which retains from the water an atom of typical hydrogen replaceable by potassium.

265. Under the action of oxidizing agents, or of molten potassic hydrate, methylic alcohol gives rise to the formation of formiates, such as hydric formiate $H C H O_2$. These formiates are analogous in their constitution to the acetates (such as hydric acetate, $H C^2 H_3 O_2$), and accordingly the two salts afford us a second instance of homology.

By limiting the action of oxidizing agents on methylic alcohol there is some reason to believe that a product of the composition $C H_2 O$, corresponding to aldehyde, has been obtained.

Four other alcohols have been found in the fermented 'mark' of the grape. This substance consists of the skins, seeds, and stalks of grapes from which the juice has been expressed for the manufacture of wine. When allowed to ferment, the mass yields vinic alcohol, which is sold as brandy; but with this brandy there is a substance known by the name of fousel oil, which comes over mostly at the end of the distillation. This fousel oil has been found

to contain propylic alcohol (HC^3H_7O), sometimes called tritylic, amylic alcohol ($HC^5H_{11}O$), and caproic alcohol ($HC^6H_{13}O$), sometimes called hexylic. Different specimens of the fousel oil contain these bodies in different proportions, and they are separated from one another by oft-repeated fractional distillations. Butylic alcohol ($C^4H_{10}O$) has been found in some specimens of fousel oil made from potato spirits, as well as from the fousel oil of beetroot molasses. The most advantageous form of apparatus for the purpose of such fractional distillations is found to be a flask with a very long neck, near the top of which is the bulb of a thermometer. The top of the neck communicates with a condenser, in which the most volatile constituents of the distilling mixture are collected; whilst the less volatile constituents are condensed in the neck of the flask, and run back into the boiling liquid.

266. Propylic Alcohol ($C^3H_8O = 2$ vols.; boiling-point, 96°). This body is not miscible with water in all proportions, although water dissolves a great deal of it. Its reactions are in all respects analogous to those of vinic alcohol, and it is considered to contain the radical propyl (C^3H_7) in the same manner that vinic alcohol contains the radical ethyle. It is therefore homologous with methylic and vinic alcohols, and is the third term of the series of alcohols. Its derivatives—propylic chloride (C^3H_7Cl), propylic iodide (C^3H_7I), propylic nitrate ($C^3H_7NO_3$), hydro-propylic sulphate ($HC^3H_7SO_4$), &c.—are homologous with the corresponding methyle and ethyle compounds.

A substance called iso-propylic alcohol of the same composition as propylic alcohol has been formed by the action of sodium amalgam upon acetone in presence of water. Acetone contains only six atoms of hydrogen in each molecule, its formula being C^3H_6O, so that the propylic alcohol is formed by the addition of two atoms of hydrogen to

acetone. The alcohol thus obtained differs in some respects from that formed from the mark. Its boiling-point is below 90°. The same product seems to be formed from acrolein by a similar treatment. Acrolein is composed of C^3H_4O, and sodium amalgam in presence of water adds to its hydrogen, forming two liquids of like composition (C^3H_8O), but differing from one another by their boiling-points—one of them boiling between 87° and 88°, while the other boils between 96° and 98°. The former of these is supposed to be identical with the product formed from acetone, and the latter identical with propylic alcohol.

The hydro-carbon propylene (C^3H_6) is absorbed rapidly by oil of vitriol, and the solution when distilled by water yields a distillate containing an alcohol of the composition C^3H_8O, and boiling at 85°.

It has been found that iso-propylic alcohol breaks up more easily into propylene and water than is the case with the propylic alcohol formed by fermentation, and it is considered probable that the alcohol made from acetone may be identical with this one made from propylene.

Normal propylic alcohol can be oxidized like vinic alcohol, yielding propylic aldehyde (C^3H_6O), a body isomeric but not identical with acetone; and by further oxidation it yields hydric propionate ($C^3H_6O_2$).

267. Iso-propylic alcohol, however, on oxidation yields acetone, and these two reactions indicate the nature of the isomerism in the two cases. Ethylic alcohol may be looked upon as an atom of methyle united with the group $H_2CO H$, and in like manner, normal propylic alcohol can be represented as an atom of ethyle united with the same group $H_2CO H$.

Thus the formula for the normal propylic alcohol will be

$$\begin{array}{l} H_3CC \quad COH \\ \quad H_2 \mid H_2 \end{array}$$

and when it is oxidized to hydric propionate, the two atoms of hydrogen of the group $H_2CO H$ are replaced by an atom of oxygen. The atom of carbon to which hydroxyl (O H) is united is only combined with one other atom of carbon.

The constitution of acetone is represented by the formula

$$H_3C\overset{O}{C}CH_3,$$

and when it is hydrogenized, the combination between the oxygen and the carbon is loosened, one atom of hydrogen being united to carbon through the intervention of oxygen, the other atom of hydrogen being united directly to the carbon, thus—

$$H_3C\overset{O}{\overset{H}{C}}CH_3.$$

Hence in isopropylic alcohol the atom of carbon to which hydroxyl is united is combined with two other atoms of carbon, and on this character, the division of alcohols into primary, secondary, and tertiary has been founded. When oxidized, primary alcohols yield acids containing the same number of atoms of carbon as they themselves contain; secondary alcohols yield bodies homologous with acetone, and tertiary alcohols yield two or more acids containing a less number of atoms of carbon than they themselves contain.

268. Butylic Alcohol ($C^4H_9.OH$). Several isomeric modifications of this alcohol are known, two of which are primary alcohols, one secondary, and one tertiary.

The normal primary alcohol has been obtained by the hydrogenization of butyric aldehyde, prepared by the distillation of a mixture of calcic formiate and normal calcic butyrate. Its constitution is represented by the formula

$$H_3C\,C\,\underset{H_2}{C}\,\underset{H_2}{C}\,COH.$$

It boils at 115°C. On oxidation it yields the normal butyrate, identical with that prepared from normal propylic cyanide.

The iso-primary butylic alcohol is prepared from the fousel oil obtained in the distillation of spirits from fermented beet-root. It boils at 109°, several degrees below the boiling-point of the normal alcohol. On oxidation it yields the iso-butyrate. Its constitution is represented thus—

$$\begin{array}{l} \quad H \\ H_3C\,C \quad C\,O\,H. \\ \quad C \;\vert\; H_2 \\ \quad H_3\vert \end{array}$$

A volatile compound of the composition $C^4H_9I = 2$ vols., boiling at 117° or 118°, has been obtained by the action of hydric iodide on erithrite ($C^4H_{10}O_4$). It has been shewn that this compound is isomeric with butylic iodide prepared from butylic alcohol. The alcohol prepared from it by the action of moist argentic oxide boils at 96°–98°. It has the constitution represented by the formula—

$$\begin{array}{l} \quad H \\ H_3C\,C \quad C\,C\,H_3 \\ \quad O \;\vert\; H_2 \\ \quad H\vert \end{array}$$

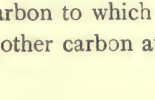
and is hence a secondary alcohol.

269. By the action of zinc-methyle on chloride of acetyle (C^2H_3OCl), a body having the empirical composition C^4H_9Cl is produced. By the action of water upon it, a body, solid at the ordinary temperature, is formed, according to the equations—

$$C^2H_3OCl + Zn(CH_3)_2 = ZnO + C^4H_9Cl;$$
$$C^4H_9Cl + H_2O = C^4H_{10}O + HCl.$$

It forms large colourless crystals, which boil at 82°. On oxidation it is converted into hydric formiate and propionate.

It is a tertiary alcohol, having the constitution represented by the explicit formula—



in which the atom of carbon to which the hydroxyl is united is combined with three other carbon atoms.

CHAPTER XXXIX.

270. Amylic Alcohol ($HC^5H_{11}O = 2$ vols.; boiling-point, 129° to 132°). This alcohol is the commonest constituent of fousel oil, and is easily obtained in quantity from that source. It has an exceedingly unpleasant odour, and is said to produce headache if much inhaled. It is dissolved by water but slightly, and it floats upon water like an oil. Potassium displaces one atom of hydrogen in amylic alcohol, forming a solution of potassic amylate ($KC^5H_{11}O$) in the alcohol. The common hydric salts decompose amylic alcohol, forming water and compounds of the radical amyle, such as amylic chloride ($C^5H_{11}Cl$), hydr-amylic sulphate ($HC^5H_{11}SO_4$), &c.; and there is no doubt that it is analogous in its constitution to the true alcohols, and contains the radical amyle C^5H_{11} in the place of one atom of hydrogen of water.

When heated with concentrated hydric sulphate amylic alcohol does not, however, yield an ether as vinic alcohol does. The mixture becomes black—gives off sulphurous and carbonic acids, together with products of the destruction of the amylic compound.

Still less does amylic alcohol yield a gas homologous with olefiant gas when heated with a greater quantity of strong hydric sulphate. When, however, amylic alcohol is mixed with zinc chloride in the proportion of $1\frac{1}{2}$ times its weight, and after standing two or three days, carefully distilled,

a mixture of volatile products is obtained, containing amylene— (C^5H_{10}=2 vols.),
which boils at 35°, and has a specific gravity of .663 at 0°. This body is proved by its reactions to be the olefiant gas of amylic alcohol, and is less volatile than olefiant gas itself in consequence of its greater molecular weight.

A mixture of oil of vitriol with one-quarter of its volume of water dissolves amylene, forming sulphamylic acid, and by diluting this liquid with water and distilling, an alcohol is formed, differing from amylic alcohol formed by fermentation by its greater tendency to break up into amylene and water.

271. Pasteur has found that in fousel oil there are two isomeric amylic alcohols; one of them rotating the ray of polarized light, boiling at 127°–128°, while the other has no rotating action upon the ray, and boils at 129°. By combining these two alcohols with hydric sulphate, and neutralizing the compound (hydr-amylic sulphate $H(C^5H_{11})SO_4$) by baryta, salts were obtained of like composition $Ba(C^5H_{11}SO_4)_2$, but differing from one another in their solubility in water; the salt made from the rotating alcohol being $2\frac{1}{2}$ times as soluble as that made from the inactive alcohol.

By the action of an aqueous solution of chromic acid mixed with hydric sulphate, fousel oil is oxidized, forming a mixture of hydric valerate ($C^5H_{10}O_2$) and valerianic aldehyde ($C^5H_{10}O$); the former, a salt homologous with the acetate and boiling at 176°, the latter, a neutral body which combines with hydro-sodic sulphite. The aldehyde boils at 96°; in contact with oxygen it is readily transformed into hydric valerate.

272. The ether of amylic alcohol (amylic oxide, $(C^5H_{11})_2O$) has been obtained by another process, and found to boil at 176°, a circumstance which sufficiently accounts for its not

being obtainable by heating a mixture of the alcohol with strong oil of vitriol, as the ether is burnt by it at a lower temperature than its boiling-point.

Amylic Ether ($C^{10}H_{22}O = 2$ vols.; boiling-point, 176°) has been prepared by the action of amylic iodide on potassic amylate—

$$C^5H_{11}I + \begin{matrix} K \\ C^5H_{11} \end{matrix} O = KI + \begin{matrix} C^5H_{11} \\ C^5H_{11} \end{matrix} O.$$

And this mode of formation leaves no doubt as to the fact that its constitution is analogous to that of the lower ethers.

Amylomethylic ether $\left(\begin{matrix} C^5H_{11} \\ C\ H_3 \end{matrix} O\right.$; boiling-point, 92°$\left.\right)$ is obtained by the action of methylic iodide on potassic amylate, or by distilling a mixture of equivalent weights of amylic and methylic alcohols with hydric sulphate, allowing the mixed alcohols to flow gradually into the boiling mixture, as vinic alcohol is allowed to flow in during the common continuous process of etherification.

Amylovinic ether $\left(\begin{matrix} C^5H_{11} \\ C^2H_5 \end{matrix} O = 2\right.$ vols.; boiling-point, 112°$\left.\right)$ has been obtained by perfectly similar processes, from the vinic and amylic alcohols.

273. The higher ethers of the alcohol series are but little known. The formation and constitution of ethers have taught us the important fact that the oxide of a monovalent element or radical contains in each molecule two monads, and that the compound of water with the oxide of a monad does not contain in each molecule the elements of one molecule of the oxide in addition to the elements of one molecule of water, but only half of that quantity.

Thus alcohol, which is truly the compound of water with ethylic oxide, $(C^2H_5)_2O$, does not contain a complete molecule of ether plus a complete molecule of water in each of its own molecules, for two molecules of alcohol must concur

to form one of ether and one of water. It is not long since chemists believed that ether and water were formed by the mere cutting in two of a molecule of alcohol; and while so representing the process, they consistently assumed that the oxygen in each molecule (weighing 16) was not one atom, but two atoms, each weighing 8. Thus using the symbol $\overset{0}{2}=8$, we should represent ether as $C^2H_5\overset{0}{2}$, water as $H\overset{0}{2}$, and alcohol as $\begin{matrix}C^2H_5\overset{0}{2}\\H\overset{0}{2}\end{matrix}$, methylic alcohol would be $\begin{matrix}CH_3\overset{0}{2}\\H\overset{0}{2}\end{matrix}$, and methylic oxide $CH_3\overset{0}{2}$: and according to this system each molecule of water, methylic oxide, or vinic oxide would occupy one volume, while each molecule of the alcohols would occupy two volumes, like a molecule of vinic or methylic iodide. The formation of common ether by the action of vinic iodide on potassic ethylate would be represented as an interchange between potassium in the one and ethyle in the other molecule; such exchange being accompanied by a breaking up of the molecule $\begin{matrix}C^2H_5\overset{0}{2}\\C^2H_5\overset{0}{2}\end{matrix}$ into two molecules of the composition $C^2H_5\overset{0}{2}$.

But this explanation would assume the occurrence of a process of breaking up, which is proved not to occur in the closely analogous case of the formation of methylo-amylic ether, by the action of methylic iodide on potassic amylate. In this case the compound $\begin{matrix}C^5H_{11}\overset{0}{2}\\CH_3\overset{0}{2}\end{matrix}$ does not break up into $C^5H_{11}\overset{0}{2}$ and $CH_3\overset{0}{2}$.

In like manner, when sulphovinic acid reacts upon alcohol, forming sulphuric acid and ether, the process would have to be represented as an interchange of ethyle in the acid with hydrogen in the alcohol, and as a breaking up of the ether into two molecules. It is found in every case in which the radical contained in the acid can be distinguished

from the radical contained in the alcohol, that the two go into the composition of one molecule of ether.

When sulphovinic acid is boiled with water an interchange of ethyle in the acid and hydrogen in the water takes place, forming hydric sulphate and alcohol; and if the molecule of water were $H\frac{O}{2}$, the process could not be explained without assuming that the ether $C^2H_5\frac{O}{2}$ combines at the moment of its formation with a molecule of water to form a molecule of alcohol.

Not only would the analogous bodies—water, alcohols, ethers, &c.—be represented in this manner by dissimilar formulæ, some containing $\frac{O}{2}$ in one molecule, others two small atoms of oxygen in each molecule—

$$H\frac{O}{2},\ CH_3\frac{O}{2},\ C^2H_5\frac{O}{2},\ C^2H_5H\frac{O}{2}\frac{O}{2},\ CH_3H\frac{O}{2}\frac{O}{2},\ \&c.;$$
$$CH_3C^2H_5\frac{O}{2}\frac{O}{2},\ C^2H_5C^5H_{11}\frac{O}{2}\frac{O}{2},\ \&c.;$$

but it would be necessary to assume, besides the interchanges which are known to take place, a number of separations and combinations among the products of these interchanges, combinations and separations which are proved to have no existence in closely analogous cases.

274. Caproic Alcohol ($HC^6H_{13}O = 2$ vols.; boiling-point, 154° to 166°) has been obtained in small quantities from the mark of the grape. By distilling mannite ($C^6H_{14}O_6$) with an aqueous solution of hydric iodide, Wanklyn has obtained a volatile oil of the composition $C^6H_{13}I = 2$ vols., from which so-called hexylic alcohol ($HC^6H_{13}O$) has been obtained isomeric with the alcohol obtained from the mark. A hydric salt of the composition $C^6H_{12}O_2$, called caprate, has been found in butter and several other fatty mixtures. It stands to caproic alcohol in the same relation in which the acetate stands to vinic alcohol—

$$C^6H_{14}O - H^2 + O = C^6H_{12}O_2.$$

Œnanthic alcohol ($C^7H_{16}O$) appears to be formed in

many cases by distilling castor-oil soap with potassic hydrate.

Its aldehyde, called œnanthol ($C^7H_{14}O$), is found among the products of the dry distillation of castor oil, and is separated from the oily products accompanying it by distilling the mixture with steam, which carries over the œnanthol accompanied by a little impurity, and a repetition of the distillation with water renders it still purer.

By the action of hydric nitrate on castor oil a volatile salt is formed, which distils over with water from the retort in which the oxidation takes place. This oily salt has the composition $C^7H_{14}O_2$, and is called hydric œnanthylate.

Caprilic alcohol ($C^8H_{18}O$=2 vols.; boiling-point, 178°) was discovered by M. Bouis in the distillation of castor-oil soap with potassic hydrate. Potassic sebate remains behind in the retort—

Potassic ricinoleate. Potassic sebate.

$$\overbrace{C^{18}H_{33}KO_3}+KH_3O_2=C^8H_{18}O+\overbrace{C^{10}H_{16}K_2O_4}+H^2.$$

Hydric caprilate ($C^8H_{18}O_2$) has been obtained from butter and from cocoa-nut oil.

275. Cetylic Alcohol ($C^{16}H_{34}O$) is derived from a beautiful crystalline compound known by the name of spermaceti, which is found with other fats in the heads of whales. Potassic hydrate melted with a little water decomposes this compound, easily forming potassic palmitate ($C^{16}H_{34}KO_2$) and cetylic alcohol. The decomposition is effected at a lower temperature by the aid of alcohol. The alcohol can be obtained by precipitating the palmitate by calcic chloride, forming calcic palmitate, which carries down the cetylic alcohol with it. Ether dissolves the alcohol, leaving the palmitate. Cetylic alcohol melts at 49°.

By distilling cetylic alcohol with phosphoric acid a hydro-

carbon of the composition $C^{16}H_{32}$ is obtained. This olefiant gas of cetylic alcohol boils at about 275°.

Spermaceti has the empirical composition $C^{32}H_{64}O_2$, and its rational formula is $\begin{matrix}C^{16}H_{31}O\\C^{16}H_{33}\end{matrix}O$, which represents it as cetylic palmitate. Potassic hydrate puts an atom of potassium into this group in lieu of an atom of the radical cetyle—

$$\begin{matrix}C^{16}H_{31}O\\C^{16}H_{33}\end{matrix}O+\begin{matrix}H\\K\end{matrix}O=\begin{matrix}C^{16}H_{31}O\\K\end{matrix}O+\begin{matrix}H\\C^{16}H_{33}\end{matrix}O.$$

Palmitic acid is the chief solid constituent of so-called palm oil, which is now so largely imported for the manufacture of soap, &c.

276. Cerotic Alcohol ($C^{27}H_{56}O$) has been prepared by Brodie from Chinese wax, by a decomposition similar to that by which cetylic alcohol was obtained from spermaceti.

Potassic cerotate ($C^{27}H_{53}KO_2$) is obtained at the same time. Cerotic alcohol is a hard and brittle solid, insoluble in water, but soluble in alcohol and ether. It melts at 97°.

A solid hydrocarbon has been obtained from Chinese wax, possessing probably the composition $C^{27}H_{54}$. It melts between 57° and 58°. In its properties this substance has some resemblance to the mixtures now so much used by the name of **Paraffine,** which are found among the products of dry distillation of boghead, or cannel coal, and various bituminous schists.

The hydric salt of cerotic acid ($C^{27}H_{54}O_2$) is found in several varieties of beeswax, and is extracted from that substance by boiling alcohol. It melts at 78°.

Melissic Alcohol ($C^{30}H_{62}O$) is the highest term now known of the alcohol series. It was prepared by Brodie from melissic palmitate $-\begin{matrix}C^{30}H_{61}\\C^{16}H_{31}O\end{matrix}O$, a constituent of beeswax, by the action of potassic hydrate.

It is partly decomposed by distillation, water being formed, together with a beautiful hydrocarbon ($C^{30}H_{60}$), which melts at 62°.

Molten potassic hydrate oxidizes melissic alcohol, forming potassic melissate with evolution of hydrogen.

$$\begin{matrix} C^{30}H_{61} \\ H \end{matrix} O + \begin{matrix} H \\ K \end{matrix} O = \begin{matrix} C^{30}H_{59}O \\ K \end{matrix} O + H^4.$$

CHAPTER XL.

277. The series of salts homologous with the acetates is usually named after that most important term, the 'acetic series.'

The first term of the series (the formiate) has been described among inorganic compounds, to which it may fairly be considered as belonging since Berthelot's synthetical formation of potassic formiate from potassic hydrate and carbonic oxide.

Hydric Acetate ($C^2H_4O_2$ = 2 vols.; boiling-point, 120°) is largely prepared in the impure state for domestic use, and sold by the name of vinegar. The process of its formation is an oxidation of alcohol in presence of water, and under the influence of an organism commonly called the vinegar plant (*mycoderma aceti*). A wort made usually from malt is subjected to alcoholic fermentation, and the 'wash,' or weak alcoholic liquid thus obtained, is allowed to settle, so that the yeast may separate from it as completely as possible. Large vats are filled to near the top with pieces of flat wicker-work like short pieces of board. The new vat full of new wicker is watered for several days with wash partially converted into vinegar in an old vat. This wash contains abundant germs of the mycoderma, and after a few days the surface of the wicker in the new vat is found covered with a growth of the plant, which goes on increasing during the subsequent use of the vat, until it nearly fills up the space between the pieces of wicker, through which the wash

must trickle. The vat and its contents are then cleared of the greater part of the organic growth, and set to work again. When a vat is in full work, a stream of wash either fresh or partially acetified is being distributed over the top of the wicker, and trickles down over it and in contact with the mycoderma. At the same time a current of air enters by holes at the bottom of the vat, and passes upwards to outlets at the top of the vat, where it escapes after giving up a part of its oxygen to the alcohol. Each molecule of alcohol combines with two atoms of oxygen, forming water and the acetate—

$$C^2H_6O + O^2 = H_2O + C^2H_4O_2.$$

The process is accompanied by the evolution of heat, and a vat with its contents, when in full work, is found to be heated to about 35°. This heat, of course, causes an upward draught of the air in the vat, which establishes the circulation necessary for a continuance of the process of oxidation.

Some of the brown vinegar obtained in this way is purified by distillation, and then sold in the form of colourless and nearly pure acetate. The brown undistilled vinegar no doubt contains the glycerine and succinate which were formed by the vinous fermentation of the wort.

Acetates are also largely prepared by the destructive distillation of wood, and a product obtained from that source is often called pyroligneous acid. The watery part of the crude distillate from wood is separated from the tar, and neutralized by lime. When this mixture is distilled, impure wood-naphtha goes over with water, and crude calcic acetate is left behind. The tarry colourless matters which at first accompany the salt are easily rendered insoluble by transforming the calcic salt into a sodic salt and heating this sodic acetate. On dissolving the acetate in water a nearly colourless solution is obtained. The hydrogen salt is obtained by

distillation of its sodic salt with hydric sulphate, or sometimes of its calcic salt with hydric chloride.

278. The pure hydric acetate is often called glacial acetic acid, from its property of crystallizing at low temperatures. It is most easily obtained on a small scale by dividing a given quantity of the dilute aqueous acid into two equal parts, neutralizing one of these by potash, then mixing with the other, and evaporating the mixture. When nearly dry, the mixture should be poured into a retort. By raising the temperature gradually the water can be completely expelled, leaving a substance of the composition $C^2 H_3 K O_2 C^2 H_4 O_2$—a compound in which potassic acetate is united with hydric acetate in a loose manner similar to that in which it unites with water of crystallization. At 200° this compound is decomposed, giving off the pure hydric salt, or glacial acetic acid. At a temperature a little above its boiling-point, the vapour density of hydric acetate corresponds to the formula $C^4 H_8 O_4$; but at higher temperatures it expands, and then corresponds to the formula $C^2 H_4 O_2$.

The acetate forms with one molecule of water a compound $C^2 H_4 O_2 H_2 O$, of which the density is 1.073. Solutions containing a greater proportion of hydric salt have a smaller specific gravity, that of the glacial acid being 1.063. More dilute solutions have also a lower density.

The metallic acetates are for the most part very soluble in water. Silver acetate ($Ag C^2 H_3 O_2$) is one of the least soluble. Ferric and aluminic acetates are decomposed by ebullition of their aqueous solution, hydric acetate being carried away by the steam, and an oxy-salt being precipitated. A similar decomposition takes place more slowly when a solution of one of these salts is spread over the surface of a cotton fabric, and hung up in a moist and warm atmosphere. This process is called 'ageing' by the cotton-printers, and it effects a deposition of ferric oxyacetate or aluminic oxyacetate

on the fibres of the cloth, while hydric acetate evaporates. This deposit of the ferric or aluminic compound is called a ' mordant.'

279. Plumbic Acetate is one of the commonest salts of the acid. It is usually known by the name ' sugar of lead.' Its crystals contain three molecules of water of crystallization; $Pb\,(C^2\,H_3\,O_2)_2\,(H_2\,O)_3$.

An aqueous solution of this salt dissolves plumbic oxide readily, and acquires thereby an alkaline reaction and the property of becoming turbid by contact with carbonic acid.

Plumbic hydro-acetate, H O. Pb O. $C^2\,H_3\,O$, appears to be formed by the action of lead oxide on the acetate; but when more oxide is employed, triplumbic dioxyacetate ($Pb_3\,O_2\,(C^2\,H_3\,O_2)_2$) is formed. A solution of this salt is used in pharmacy by the name of ' goulard water.'

Copper acetates are formed by exposure of metallic copper, together with vinegar, to the air. They are popularly called ' verdigris.' There is not only a normal cupric acetate ($Cu\,(C^2\,H_3\,O_2)_2$), but also a cupric hydro-acetate ($Cu\,H\,O\,C^2\,H_3\,O_2$).

The name ' emerald green' is given to a beautiful cupric aceto-arsenite of the composition $O_2\,As\,Cu\,O\,C^2\,H_3\,O$.

Acetates are also obtained containing the alcohol radicals. These bodies are of the class called **Compound Ethers.** They are formed, together with water, by heating the hydric salt with the alcohol, but the presence of hydric sulphate or chloride is found to accelerate greatly the process of combination. When thus used, the acid mineral salt is termed an etherifying agent. The action of hydric sulphate is, no doubt, of the same kind as in the formation of ether and water from alcohol; viz. first, the formation of sulphovinic acid and water, then by the action of sulphovinic acid on the acetate the formation of acetic ether and the reproduction of the sulphate—

$H C^2 H_5 S O_4 + H O C^2 H_3 O = C^2 H_5 . O . C^2 H_3 O + H_2 S O_4$.
like $H C^2 H_5 S O_4 + H O C^2 H_5 = C^2 H_5 . O . C^2 H_5 + H_2 S O_4$.

Acetic Ether ($C^2 H_5 O C^2 H_3 O$) has an agreeable odour, by which its presence can be detected when it is not mixed with other odorous bodies. Its boiling-point is 74°, whilst that of methylic acetate is 58°, butylic acetate 114°, and amylic acetate boils at 125°. Mixtures of these ethers, and of others containing homologues of the acetate, are no doubt present in various small proportions in wines, and contribute to their characteristic 'bouquet.'

Acetic ether is decomposed by ammonia, forming alcohol and acetamide—

$$\begin{matrix} C^2 H_5 \\ C^2 H_3 O \end{matrix} O + N H_3 = \begin{matrix} C^2 H_5 \\ H \end{matrix} O + N H_2 (C^2 H_3 O).$$

280. The acetate is decomposed by chlorine under the influence of sunshine. Three products of substitution have been prepared, viz. chlor-acetate, $C^2 H_2 Cl O (O H)$, di-chlor-acetate, $C^2 H Cl_2 O (O H)$, and tri-chlor-acetate, $C^2 Cl_3 O (O H)$. They are monobasic, like the acetate itself, though no doubt stronger.

A **Thi-acetate** is a compound formed by the action of phosphoric sulphide on the acetate, probably thus first—

$$C^2 H_3 O (O H) + P_2 S_5 = C^2 H_3 O (S H) + P_2 S_4 O.$$

It boils at 93°.

A sulph-acetate is formed by the action of sulphuric acid ($S O_3$) on the acetate. Its formation is analogous to that of sulphovinic acid, for it contains the elements of a molecule of hydric acetate in addition to those of a molecule of sulphuric acid—

$$C^2 H_3 O (O H) + S O_3 = C^2 H_3 O H S O_4 .$$

It forms a potash salt of the empirical formula $C^2 H_2 K_2 S O_5$, and a baryta salt $C^2 H_2 Ba S O_5$, which is slightly soluble in water.

281. Phosphoric chloride decomposes hydric acetate, exactly in the same manner as it decomposes alcohol, forming chloro-phosphoric acid, hydric chloride, and the chloride of the radical acetyl (C^2H_3O),—

$$H\,O\,C^2H_3O + P\,Cl_5 = P\,O\,Cl_3 + H\,Cl + Cl\,C^2H_3O.$$

The action is exceedingly energetic, and the acetic chloride can be distilled over at a gentle heat, leaving the greater part of the chloro-phosphoric acid behind.

Acetic Chloride ($Cl\,C^2H_3O$) is a liquid heavier than water, and boiling at 55°. It has a very pungent odour, and in contact with moisture it is rapidly decomposed, forming hydric chloride and acetate—

$$Cl\,C^2H_3O + H\,O\,H = H\,O\,C^2H_3O + H\,Cl.$$

In this decomposition the acetate is formed by replacing one atom of hydrogen in water by an atom of acetyl, or by replacing the atom of chlorine in acetic chloride by hydroxyl ($H\,O$).

In contact with alcohol, acetic chloride forms hydric chloride and acetic ether—

$$H\,O\,C^2H_5 + Cl\,C^2H_3O = C^2H_5.O.C^2H_3O + H\,Cl.$$

With potassic acetate it forms acetic acid ($(C^2H_3O)_2O$), by replacing the potassium in the salt by acetyl—

$$Cl\,C^2H_3O + K\,O\,C^2H_3O = (C^2H_3O)_2O + K\,Cl.$$

According to this reaction, acetic acid is a molecule of water in which the two atoms of hydrogen are replaced by two atoms of acetyl; the hydrate being a molecule of water in which one atom of hydrogen is replaced by one of acetyl.

Acetic acid boils at 138°. It sinks in water, and does not appear to dissolve in it as such. It, however, gradually decomposes the water, forming two molecules of hydric acetate—

$$C^2H_3O.O.C^2H_3O + HOH = C^2H_3O.OH + HO.C^2H_3O.$$

Phosphoric chloride decomposes acetic acid, forming chloro-phosphoric acid and acetic chloride—

$$(C^2H_3O)_2O + PCl_5 = POCl_3 + 2\,ClC^2H_3O.$$

282. Acetic chloride reacts very violently on ammonia, removing one atom of hydrogen from a molecule of the volatile alkali, and replacing it by an atom of acetyl—

$$ClC^2H_3O + 2\,NH_3 = H_2NC^2H_3O + NH_4Cl.$$

This ammonia, containing acetyl in the place of one atom of hydrogen, is called **Acetamide.** It is also obtained by heating ammonic acetate, so as to remove half the oxygen of that salt in combination with hydrogen—

$$(NH_4)OC^2H_3O = H_2NC^2H_3O + H_2O.$$

Acetamide is also formed when ammonia acts on acetic ether—

$$C^2H_3O.O.C^2H_5 + NH_3 = H_2N.C^2H_3O + HOC^2H_5.$$

It is a crystalline solid, having very nearly neutral properties; for, on the one hand, it combines freely with hydric nitrate or chloride; on the other hand, it is decomposed by potassium, with evolution of hydrogen and formation of a weak salt. Products formed like acetamide by the replacement of hydrogen in ammonia by a radical of chlorous properties are called amides. Acetamide is a primary amide. When two atoms of hydrogen are so replaced, as in di-acetamide, $(C^2H_3O)_2NH$, the compound is termed a secondary amide, and tertiary amides are single molecules of ammonia, in which all the typical hydrogen is replaced by chlorous radicals.

There are also ammonias in which the typical hydrogen is replaced partly by basylous radicals, such as the alcohol radicals; partly by chlorous radicals. Thus by the action of acetic acid on cyanic ether may be prepared an ammonia containing two atoms of acetyl and one of ethyle—

$$OCNC^2H_5 + (C^2H_3O)_2O = CO_2 + (C^2H_3O)_2NC^2H_5.$$

283. Formiates do not yield similar products to acetates.

When acted on by phosphoric chloride, the formic chloride breaks up into carbonic oxide and hydric chloride—

$$H C O . O H + P Cl_5 = P O Cl_3 + 2 H Cl + C O.$$

When phosgene is passed into absolute alcohol, a body having the composition $Cl C O . O C^2 H_5$ is formed, according to the equation—

$$Cl_2 C O + H O C^2 H_5 = Cl C O . O C^2 H_5 + H Cl.$$

By the action of hydric formiate on alcohol, ethylic formiate, $H C O . O C^2 H_5$, is produced, and a comparison of this formula with that of the body produced from phosgene, shews that the latter is to be considered as chloro-formic ether, that is, formic ether in which the atom of hydrogen in formyl (H C O) is replaced by an atom of chlorine.

Formic acid, $(H C O)_2 O$, has not been obtained. Propionates, butyrates, valerates, and the higher terms of this series, all yield chlorides homologous with acetic chloride; and these chlorides, in their turn, react like acetic chloride on the corresponding potassium salts, forming propionic acid, $(C^3 H_5 O)_2 O$, butyric acid, $(C^4 H_7 O)_2 O$, valerianic acid, $(C^5 H_9 O)_2 O$, &c.

CHAPTER XLI.

284. Propionic Acid ($C^3 H_5 O . O H$) has obtained its name from the circumstance of its being the first acid of the series which can be precipitated, like an oily compound, from its aqueous solution by calcic chloride or glacial phosphoric acid. A propionate is best obtained by the action of potash on vinic cyanide—

$$C^2 H_5 C N + H_3 K O_2 = C^3 H_5 K O_2 + N H_3.$$

Butyrates were first obtained by Chevreul from the constituents of butter. They are most advantageously prepared by leaving calcic lactate with water and old cheese at a temperature of 35°. Hydrogen and carbonic acid are given off during the process of fermentation which takes place, and the lactate is entirely destroyed, a butyrate being formed in its place. Acetates and valerates are frequently formed in smaller quantity at the same time.

Hydric butyrate ($C^4 H_7 O . O H$) boils at 159°. Its density is 0.9886 at 0°C. It dissolves in water in all proportions. Its metallic derivatives are in general soluble in water. It forms ethers, each of them boiling at a higher temperature than the corresponding acetate. They are also less soluble in water than the acetic ethers.

285. Hydric Valerate ($C^5 H_{10} O_2$; boiling-point, 175°–180°; sp. gr. 0.937). This acid salt has obtained its name from the valerian root from which it was extracted. It is present in rancid cheese and in many other decomposed

organic mixtures. It is best obtained by the action of amylic alcohol on a solution of potassic dichromate acidulated by hydric sulphate. On distilling the mixture an acid distillate is obtained containing valerianic aldehyde and the valerate, which can easily be separated by potash. The valerate requires about thirty volumes of water for its solution; and when added in greater quantity, the salt floats as an oily stratum upon the aqueous solution. The oily stratum is a compound of valerate with a molecule of water ($C^5 H_{10} O_2 H_2 O$), having a density greater than that of the salt itself, viz. 0.95.

Valerates have an exceedingly persistent and unpleasant odour.

The **Caproate** ($C^6 H_{12} O_2$) was obtained from the liquid part of cow's butter. Butter was melted, and pressed after cooling. The solid crystalline residue, consisting of the glycerine derivatives of margaric and other solid acids, was put aside, and the liquid portion was dissolved in potash by the aid of heat, or, as it is called, saponified. The aqueous solution of the soap was precipitated by salt, and the soap thus obtained was decomposed by dilute hydric sulphate, and distilled. In this manner an acid distillate was obtained, consisting of water holding several hydric salts in solution, and having oily drops of acid floating upon it. The mixture was neutralized by baryta-water, and the baric salts thus obtained were separated by crystallization. In this manner a butyrate, caproate, caprilate, and caprate were obtained, the butyrate being the most soluble in water, and the solubility of the others diminishing with the increase of their molecular weight.

Hydric caproate boils at about 198°. It is most easily obtained by the decomposition of amylic cyanide. The next term of the series, viz. the œnanthylate ($C^7 H_{14} O_2$), is obtained by distilling castor oil with hydric nitrate. The

œnanthylate comes over with the vapour of water, and is collected in the receiver.

Hydric Caprilate ($C^8H_{16}O_2$; boiling-point, 236°–240°) is most conveniently prepared from cocoa-nut oil.

Hydric Pelargonate ($C^9H_{18}O_2$; boiling-point, 260°) was first prepared from geranium-leaves. Gerhardt recommends oil of rue for its preparation. This oil is distilled with dilute hydric nitrate, and the distillate neutralized by baryta and crystallized. Ethylic pelargonate appears to be the chief constituent of the so-called oil of wine—a fragrant oil which is used for flavouring purposes. The hydrogen salt of capric or rutic acid ($C^{10}H_{20}O_2$) has been found in the fousel oil of whiskey. Its baryta salt ($Ba(C^{10}H_{19}O_2)_2$) is purified by repeated crystallizations and then decomposed by sodic carbonate. The addition of dilute hydric sulphate to the sodic salt precipitates the hydrogen salt in the solid form.

Laurate ($C^{12}H_{24}O_2$) melts at 42° or 43°.

Cocinate ($C^{13}H_{26}O_2$) is said to have been obtained by saponifying cocoa-nut oil, and decomposing the soap by hydric chloride. In this manner an oily mixture of hydric salts is obtained, from which cocinate crystallizes out. The liquid constituents are pressed out from the mass by a hydraulic press. The impure cocinate thus obtained is dissolved in hot alcohol, and purified by repeated crystallizations. It is ultimately obtained with a melting-point of 42° to 43°.

There seems some reason to believe that the acid substance thus obtained was a mixture.

Myristate ($C^{14}H_{28}O_2$) melts at 49°.

The next term of the series is called benic acid. The hydrate is represented by the formula $C^{15}H_{30}O_2$.

286. Hydric Palmitate or **Cetylate** ($C^{16}H_{32}O_2$) melts at 62°. It is obtained from palm oil in the same way as the

cocinate from cocoa-nut oil, or from spermaceti after decomposition by alcoholic potash. The palmitate is frequently used for the manufacture of so-called composition candles. For this purpose palm oil can be decomposed by the action of hydric sulphate, and purified by distillation in superheated steam. It has, however, been found that the palm oil is decomposed by the action of superheated steam into hydrated acids and glycerine. These products are condensed from the steam, and the liquid hydrates removed by the action of a powerful hydraulic press from the palmitic and other solid hydrates. Water heated to a high temperature in a Papin's digester likewise decomposes palm oil and most other fats.

Hydric Margarate ($C^{17} H_{34} O_2$) was supposed to be obtained from many common oils and fats, such as olive oil, butter, goose fat, human fat, &c., by decomposition of its glycerine derivative.

Its melting-point is given at 60°, but according to analogy it ought to be higher than 62°, the melting-point of the palmitate, instead of lower. There seems some reason to suspect that what has passed for margarate is a mixture of palmitate with stearate. The former of these melts at 62° and the latter at 69° or 70°, but a mixture of the two has been found to melt at as low a temperature as 54°, and mixtures containing greater proportions of the stearate melt at higher temperatures.

A substance possessing the composition of the margarate has been made by the action of potassic hydrate on cetylic cyanide—

$$C^{16} H_{33} C N + H_3 K O_2 = C^{17} H_{33} K O_2 + N H_3.$$

The hydrogen salt made from this melts below 60°.

287. Hydric Stearate ($C^{18} H_{36} O_2$) is obtained from beef and mutton suet, together with glycerine. To obtain a stearate in a state of purity from a mixture in which it is accompanied by homologues of lower atomic weight, Heintz's

process of partial precipitation should be resorted to. This process consists in dissolving in alcohol the soap containing the stearate, and adding to the solution at the temperature of ebullition an alcoholic solution of baric or magnesic acetate in very small quantity. A stearate is under these circumstances precipitated before a palmitate or other salt containing less carbon in its molecule, and if the quantity of acetate employed be small enough, no palmitate or lower term of the series goes down with the stearate.

The stearate crystallizes in shining needles. It decomposes alkaline carbonates with effervescence, forming a so-called soap. Potassic and sodic stearates are very soluble in water, and are alkaline to test-paper. Water saturated with sodic chloride does not dissolve soaps, and the addition of salt precipitates soap from its solution. Solutions of alkaline stearates are decomposed on dilution into alkali, and hydric salt, which is precipitated together with an equivalent of the soap. The compounds with the alkaline earths and heavy metallic oxides are insoluble in water. The potash and soda salts dissolve in alcohol, but not in ether.

Hydric stearate is insoluble in water, but dissolves in alcohol, and the solution has an acid reaction to test-paper.

Other hydric salts are—

Arachidate .... $C^{20}H_{40}O_2$,	Cerotate ..... $C^{27}H_{54}O_2$,
Behenate ..... $C^{22}H_{44}O_2$,	Melissate ..... $C^{30}H_{60}O_2$.
Hyenate..... $C^{25}H_{50}O_2$,	

The hyenate has been found in the fat of the hyæna. It melts at 77° or 78°. Derivatives of the cerotate are contained in bees'-wax, and the hydrate can be dissolved out from it by alcohol. Its melting-point is given at 78°.

Hydric melissate has been obtained from melissic alcohol by fusion with potash. It melts at 88°–89°.

All the salts of this series, frequently called the adipic series, are oxidized by boiling hydric nitrate. Two classes of products are formed in the process—viz. lower hydric salts of the same series, such as caproate, œnanthate, caprilate, &c., which pass over into the receiver, and salts homologous with the oxalate, which remain in the retort.

288. Aldehydes are a class of bodies analogous in their properties to common vinic aldehyde (C^2H_4O). They are a little superior to alcohols in their power of combining with bases; thus common aldehyde when dissolved in ether absorbs ammonia, and forms a crystalline compound possessing the composition $C^2H_3NH_4O$. Aldehydes absorb oxygen very freely, forming acid hydrogen salts, such as the acetate ($C^2H_4O_2$), formed by the absorption of an atom of oxygen by vinic aldehyde. Another important property is that of combining with hydro-sodic sulphate, forming compounds which are soluble in water, but insoluble or nearly so in a saturated aqueous solution of the double sulphite.

Vinic Aldehyde (C^2H_4O = 2 vols.; boiling-point, 21°; sp. gr. 0.8) is usually prepared by the action of a mixture of hydric sulphate and red chromate on alcohol. The impure distillate is rectified at a gentle heat over calcic chloride, and what comes over is mixed with dry ether and precipitated in combination with ammonia by passing that gas into the solution. This ammonia compound is easily decomposed by dilute hydric sulphate.

It is also formed by the dry distillation of an acetate and a formiate—

$$C^2H_3O.OK + HCO.OK = C^2H_3O.H + CO(OK)_2,$$

the hydrogen of the formiate replacing the group (OK) in the acetate. Thus the explicit formula of aldehyde is

$$H_3CCH$$
$$\quad\quad O$$

Aldehyde is also formed by the destructive distillation of hydric lactate—

$$C^3 H_6 O_3 = C^2 H_4 O + C O + H_2 O.$$

It is a very volatile liquid which mixes in all proportions with water, and its solution reduces metallic silver in the form of a bright mirror from a solution of the nitrate, neutralized by ammonia. Caustic potash decomposes aldehyde, forming a brown resinous substance, whilst potassic acetate and formiate are produced. The compound formed by combination of aldehyde with hydro-sodic sulphite has the composition $C^2 H_3 Na S O_3$.

Vinic aldehyde is remarkable for the variety of isomeric bodies formed from it under various conditions. Four of these have been described; two of them being liquids very different from aldehydes in their properties, and two of them being solids.

An aqueous solution of aldehyde is decomposed by sulphuretted hydrogen, forming the compound $C^2 H_4 S$.

Chlorine gas passed to saturation into alcohol forms amongst other products a body called chloral. **Chloral** is chlorinated aldehyde, having the composition $C^2 H Cl_3 O$. It is oxidized by hydric nitrate, yielding hydric chloracetate ($C^2 Cl_3 H O_2$). By the action of potash it yields chloroform and potassic formiate—

$$C^2 Cl_3 H O + H O K = C Cl_3 H + H C O . O K.$$

289. Acetone is a compound resembling aldehyde in several of its properties, and a numerous class of bodies of the same family as acetone have similar resemblances to aldehydes. This class of bodies, like acetone, is called the ketone family.

Acetone ($C^3 H_6 O = 2$ vols.; boiling-point, 55°; sp. gr. 0.8) is a constituent of wood spirit. It is easily obtained in a state of purity by distilling sodic acetate. Two molecules

of the salt react on one another, forming sodic carbonate and acetone—

$$2\,C^2H_3NaO_2 = Na_2CO_3 + C^3H_6O.$$

Acetone is a neutral liquid of an agreeable odour. It mixes in all proportions with water, but is precipitated from this solution in the form of a light oil by saturating the water with potash. Alcohol is not precipitated from its aqueous solution by potash. Acetone combines like an aldehyde with hydro-sodic sulphite, and the compound has properties analogous to those of the corresponding aldehyde compound.

Potassic hydrate decomposes the vapour of acetone, forming potassic acetate and marsh gas—

$$C^2H_3OCH_3 + KOH = C^2H_3O.OK + CH_4.$$

This reaction assimilates acetone to aldehyde, which under similar circumstances forms potassic acetate and free hydrogen—

$$C^2H_3O.H + KOH = C^2H_3O.OK + H^2.$$

The formation of acetone from two molecules of monatomic acetate favours the view that its molecule is formed by the union of an atom of methyl with an atom of acetyle, C^2H_3O. For if we arrange the elements of one molecule of potassic acetate in two groups thus—$(C^2H_3O)(OK)$, and the elements of another molecule in two other groups thus—$(CH_3)(CO.OK)$, it is evident that a double decomposition between the two will give us the compounds actually found to be formed—

$$(C^2H_3O)(OK) + (CH_3)(CO.OK) = (C^2H_3O)(CH_3) + (CO.OK)(OK).$$

Under the influence of most reagents, acetone does not, however, break up in accordance with this view of its constitution. Thus hydric chloride or phosphoric chloride gives rise to the formation of a chloride called mesitylic chloride (C^3H_5Cl). Hydric sulphate forms amongst other products

the hydrocarbon mesitylene (C^9H_{12}). Another product is the so-called mesitylic oxide ($C^6H_{10}O$), which has been considered as the ether of acetone.

When a mixture of two salts homologous with the acetates is distilled, a ketone is built up partly from the elements of one molecule, partly from those of the other. Thus a mixture of an acetate and a valerate distilled together gives rise to the formation of a ketone—

$$C^5H_9O.OK + CH_3.COOK = C^5H_9O.CH_3 + CO(OK)_2.$$

The formation of aldehydes by the distillation of a formiate with another salt is a particular class of cases belonging to this general reaction.

290. Besides the alcohols homologous with vinic alcohol, others have been obtained, containing monovalent hydrocarbon radicals with a smaller proportion of hydrogen. Thus the heavy oil (C^3H_5I) formed by the action of phosphorous iodide on glycerine, has been found to react in many respects like vinic iodide. With argentic oxalate it forms argentic iodide and a liquid of the composition $(C^3H_5)_2C^2O_4$, which behaves as an oxalate containing the radical allyle, C^3H_5, as a metal. Ammonia gas decomposes this oxalate, forming oxamide and allylic alcohol, $C^3H_5.OH$, a liquid boiling at 103°—

$$(C^3H_5)_2C^2O_4 + 2NH_3 = C^2O_2(NH_2)_2 + 2C^3H_5OH.$$

By the action of potassium on this alcohol the compound C^3H_5OK was obtained; and allylic iodide replaces the potassium by allyle forming allylic ether—

$(C^3H_5)_2O$; boiling-point, 82°.

Allylic sulphide, $(C^3H_5)_2S$, has also been prepared, and found to be identical with the essential oil of garlic.

Allylic sulpho-cyanate (C^3H_5CNS) is obtained by the action of allylic iodide on potassic sulphocyanate. It is identical with the essential oil of mustard.

CHAPTER XLII.

291. Diatomic Alcohols are compounds formed on the type of two molecules of water; an atom of a hydrocarbon replacing two atoms of hydrogen in them, one in one molecule of water, the other in the other molecule. Ethylene (C^2H_4) is a hydrocarbon, of which one atom is capable of replacing two atoms of hydrogen, or of combining with two atoms of chlorine. A molecule of ethylenic bromide ($C^2H_4Br_2$) reacts on two molecules of argentic acetate, forming argentic bromide and ethylenic acetate—

$$C^2H_4Br_2 + 2\,C^2H_3O.OAg = 2\,AgBr + C^2H_4(C^2H_3O_2)_2.$$

The reaction is parallel to that of zinc bromide ($ZnBr_2$) on argentic acetate, an atom of zinc forming the acetate $Zn(C^2H_3O_2)_2$, just as an atom of ethylene forms ethylenic acetate ($C^2H_4(C^2H_3O_2)_2$).

By the action of potash on this acetate the ethylenic hydrate is obtained $C^2H_4(HO)_2$, in the form of a liquid, soluble in water in all proportions, and having a sweet taste. It distils without decomposition at 197·5°.

This remarkable body was named **Glycol** by its discoverer Würtz. With monobasic hydric salts it forms two classes of salts.

Thus hydric chloride forms ethylenic hydrochloride, $C^2H_4Cl(OH)$, and by the action of phosphoric chloride on this body the normal chloride $C^2H_4Cl_2$ is obtained, just as the divalent radical SO_2 of the sulphates forms not only

the normal hydrate $S O_2 (H O)_2$, but also by the action of phosphoric chloride the hydrochloride $S O_2 Cl (O H)$, and the normal chloride $S O_2 Cl_2$.

With acetic acid, glycol forms the normal ethylenic acetate $C^2 H_4 (C^2 H_3 O_2)_2$, and also ethylenic hydro-acetate—

$$C^2 H_4 (H O) (C^2 H_3 O_2).$$

Sodium decomposes glycol, with evolution of hydrogen, forming in the first instance the compound

$$C^2 H_4 (O Na) (O H).$$

By prolonged heating with sodium the second atom of typical hydrogen is with difficulty expelled, forming the compound $C^2 H_4 (O Na)_2$.

292. Ethylenic Oxide ($C^2 H_4 O$) has not been obtained by processes similar to those by which ethylic oxide is obtained from alcohol. Zinc chloride decomposes glycol with the aid of heat, forming vinic aldehyde, isomeric with ethylenic oxide. The oxide has been prepared by the action of potash on the ethylenic hydrochloride. This compound breaks up into hydric chloride and ethylenic oxide—

$$C^2 H_4 Cl (O H) = H Cl + C^2 H_4 O.$$

In this respect it differs from its prototype, sulphuric hydrochloride, which breaks up into sulphuric hydrate and sulphuric chloride.

Ethylenic oxide boils at 13.5°. By heating in a closed vessel with water it reproduces glycol. Some of the oxide combines in the process with water in the proportion of two molecules of ethylenic oxide to one of water, forming the compound $(C^2 H_4)_2 O (H O)_2$, called diethylenic glycol.

293. When ethylenic bromide is heated with glycol this same compound is obtained together with triethylenic glycol, $\begin{matrix}(C^2 H_4)_3 \\ H_2\end{matrix} O_4$, tetrethylenic glycol, $\begin{matrix}(C^2 H_4)_4 \\ H_2\end{matrix} O_5$, pentethylenic glycol, $\begin{matrix}(C^2 H_4)_5 \\ H_2\end{matrix} O_6$, and hexethylenic glycol, $\begin{matrix}(C^2 H_4)_6 \\ H_2\end{matrix} O_7$.

These **Polyethylenic Glycols** are analogous to glycol itself in their reactions. But the addition of each molecule of ethylenic oxide raises the boiling-point of the glycol.

Propylenic bromide forms a glycol by the same processes which serve to prepare ethylenic glycol.

Propylenic hydrate ($C^3H_6(HO)_2$) boils however at a lower temperature than ethylenic hydrate—viz. at 188°.

Butylenic glycol ($C^4H_{10}O_2$) boils still lower—viz. at 183° to 184°.

Amylenic glycol ($C^5H_{12}O_2$) boils lowest of the four—viz. at 177°.

Methylenic glycol (CH_4O_2) has not been obtained.

Methylenic acetate ($CH_2(C^2H_3O_2)_2$) is obtained by the action of methylenic iodide on argentic acetate. It is decomposed by water into hydric acetate and a solid body melting at 152° and isomeric with methylenic oxide—

$$2\,\begin{matrix}CH_2\\(C^2H_3O)_2\end{matrix}O_2 + 2\,H_2O = \begin{matrix}CH_2\\CH_2\end{matrix}O_2 + 4\,\begin{matrix}C^2H^3O\\H\end{matrix}O.$$

Ethylenic sulphydrate ($C^2H_4(HS)_2$) was obtained many years ago by Löwig, by decomposing ethylenic bromide by an alcoholic solution of potassic sulphydrate—

$$C^2H_4Br_2 + 2\,KSH = C^2H_4(HS)_2 + 2\,KBr.$$

It combines readily with mercuric oxide, as the monatomic mercaptans do.

294. When cautiously oxidized, glycol gives rise to the formation of an acid called **Hydric Glycollate**. The reaction is perfectly similar to the formation of acetate by the oxidation of alcohol—

$$C^2H_4(HO)_2 + O^2 = CH_2(OH).(COOH) + H_2O.$$

A glycollate is also obtained by the action of potassic hydrate at a high temperature on potassic chlor-acetate—

$$KHO + C^2H_2ClKO_2 = KCl + CH_2(OH).COKO.$$

When potassic chlor-acetate is heated by itself, glycollic acid is formed—

$$C^2H_2ClKO_2 = ClK + C^2H_2O_2.$$

The glycollates are monobasic, forming only normal salts, such as $KC^2H_3O_3$, $Ba(C^2H_3O_3)_2$, &c.

When further oxidized glycol yields oxalate—

$$C^2H_4(HO)_2 + 2O^2 = C^2O_2(HO)_2 + 2H_2O;$$

and glycollates are easily oxidized, forming oxalates.

It is worthy of note that the oxalate, having two atoms of oxygen in its radical (C^2O_2), is dibasic, whereas the glycollate, having one atom of oxygen in its radical (C^2H_2O), is monobasic.

Under the influence of nascent hydrogen an oxalate has been reduced to a glycollate.

The two salts which stand to propylic glycol in the same relation as glycollate and oxalate stand to glycol, are lactate ($C^3H_6O_3$), homologous with glycollate, and malonate ($C^3H_4O_4$), homologous with oxalate.

295. Lactates, such as the hydric lactate ($C^3H_6O_3$), have obtained their name from the circumstance of being formed from the sugar of milk, by the spontaneous decomposition of milk when exposed to the air. Milk is well known to 'turn sour' on keeping, and at the same time to become thick by the formation of a solid precipitate of caseine. Salts isomeric with the lactates are present in many animal fluids. They are called sarkolactates.

Lactates are most easily obtained in quantity by the lactic fermentation of sugar. This change takes place when sugar is dissolved in water and mixed with powdered cheese, the mixture being kept at a temperature of about 30°, and the free hydric salt neutralized in proportion as it is formed. The best way to keep the liquid neutral is to put into it calcic carbonate, when calcic lactate is formed, and can be purified by recrystallization.

When carefully heated to 130° or 140°, hydric lactate decomposes in part into water and lactic acid ($C^3 H_4 O_2$). Some of this acid decomposes into aldehyde and carbonic oxide ($C^3 H_4 O_2 = C^2 H_4 O + C O$).

Phosphoric chloride forms with lactates the lactic chloride $C^3 H_4 O Cl_2$, and when partially decomposed by an alkaline hydrate this chloride forms a chloro-propionate—

$$C^3 H_4 O Cl_2 + H K O = C^3 H_4 Cl K O_2 + H Cl.$$

By the action of nascent hydrogen the chlorine can be removed from this salt and replaced by hydrogen, forming a common propionate. Lactate is easily reduced to propionate by the action of strong hydric iodide—

$$C^3 H_6 O_3 + 2 H I = C^3 H_6 O_2 + H_2 O + I^2.$$

Acetonate ($C^4 H_8 O_3$) is in its composition homologous with lactate, but has not as yet been much studied. It is made by adding to acetone the elements of the formiate, by the action of hydric chloride on prussic acid in presence of water—

$$C^3 H_6 O + C N H + 2 H_2 O + H Cl = C^4 H_8 O_3 + Cl N H_4.$$

Butylactic and oxybutyric acids are names given to acids of the same composition as acetonic acid.

Hydrated leucic acid ($C^6 H_{12} O_3$) has been obtained from a crystalline amide called leucine by the action of nitrous acid.

A body of the same composition has been obtained by Frankland and Duppa from vinic oxalate. One atom of oxygen in the radical of the oxalate is replaced by two atoms of ethyle—

$$C^2 O_2 (C^2 H_5 O)_2 + 2 C^2 H_5 - O = C^2 O (C^2 H_5)_2 (O C^2 H_5)_2.$$

From this leucic ether other salts of the acid are prepared. A similar process has been applied by the same chemists to the preparation of other terms of the series, such as—

$$C^5 H_{10} O_3 = \overset{H_2}{C^2 (C H_3) (C^2 H_5) O} O_2.$$

The substitutions are effected by the action of metallic zinc on oxalic ether mixed with vinic iodide or methylic iodide, &c., or a mixture of iodides. There are also some salts which differ from those of the aromatic series by containing one atom of oxygen in each molecule beyond the elements of the aromatic acids. These are—

Hydrated oxybenzoic acid ($C^7 H_6 O_3$),
Hydrated oxytolulic acid ($C^8 H_8 O_3$),
Hydrated phloretic acid ($C^9 H_{10} O_3$),
Hydrated oxycuminic acid ($C^{10} H_{12} O_3$).

296. Another series of diatomic salts is the oxalic series. Each molecule of these hydrogen salts forms a neutral salt with potassium, containing two atoms of the metal, and a double salt containing an atom of hydrogen and an atom of potassium, having a decidedly acid reaction. The salts are accordingly considered as dibasic. These hydrogen salts are—

Hydric oxalate ($C^2 O_2 (H O)_2$),
Hydric malonate ($C^3 H_2 O_2 (H O)_2$),
Hydric succinate ($C^4 H_4 O_2 (H O)_2$),
Hydric lipate ($C^5 H_8 O_2 (H O)_2$),
Hydric adipate ($C^6 H_8 O_2 (H O)_2$),
Hydric pimulate ($C^7 H_{10} O_2 (H O)_2$),
Hydric suberate ($C^8 H_{12} O_2 (H O)_2$),
Hydric anchoate ($C^9 H_{14} O_2 (H O)_2$),
Hydric sebate ($C^{10} H_{16} O_2 (H O)_2$).

The oxalate has been described among the simplest compounds of carbon. Hydric malonate is but little known as yet. It has been obtained by the oxidation of hydric malate, and by the action of caustic potash on cyan-acetic acid—

$$C^2 H_2 C N O.O K + H_3 K O_2 = C^3 H_2 O_2 (O K)_2 + N H_3.$$

Also by the oxidation of a sarkolactate.

Hydric Succinate ($C^4 H_6 O_4$) is among the products of the dry distillation of amber. It is formed by the action

of the nitrate on salts of the adipic series, such as butyrates—

$$C^4 H_8 O_2 + 3\,O = C^4 H_6 O_4 + H_2 O.$$

In many processes of fermentation it is one of the secondary products, and in the fermentation of a malate it is one of the chief products. It is formed by the action of hydric iodide on a tartrate—

$$C^4 H_6 O_6 + 4\,H I = C^4 H_6 O_4 + 2\,H_2 O + 4\,I.$$

Also by the same treatment of a malate—

$$C^4 H_6 O_5 + 2\,H I = C^4 H_6 O_4 + (H_2 O) + I^2.$$

Succinates have been built up from ethylene and cyanogen. Ethylenic cyanide is decomposed by potash, forming succinate—

$$C^2 H_4 (C N)_2 + 2\,H_3 K O_2 = C^4 H_4 K_2 O_4 + 2\,N H_3.$$

Hydric succinate dissolves readily in water with a decidedly acid reaction. When subjected to dry distillation it decomposes into water and succinic acid—

$$C^4 H_6 O_4 = C^4 H_4 O_3 + H_2 O.$$

Phosphoric chloride decomposes the succinate, forming the acid, hydric chloride, and phosphoric oxychloride. The further action of phosphoric chloride decomposes the acid, forming succinic chloride—

$$C^4 H_4 O_3 + P Cl_5 = C^4 H_4 O_2 Cl_2 + P O Cl_3.$$

Calcic succinate ($C^4 H_4 Ca O_4$) is soluble in water. The hydro-calcic succinate ($Ca H_2 (C^4 H_4 O_4)_2$) is a crystallizable salt.

Baric succinate ($C^4 H_4 Ba O_4$) is but slightly soluble in water, and it is insoluble in a mixture of ammonia and alcohol.

Ferric succinate is insoluble in water but soluble in hydric salts.

Succinic ether is decomposed by ammonia, forming succinamide—

$$C^4 H_4 (C^2 H_5)_2 O_4 + 2\,N H_3 = C^4 H_4 O_2 (N H_2)_2 + 2\,C^2 H_6 O.$$

There is also a class of salts called succinamates, derivable by a similar reaction from hydro-vinic succinate—

$$C^4H_4O_2(HO)(EtO) + 2NH_3 = C^4H_4O_2(ONH_4)(NH_2) + + C^2H_6O.$$

Succinic acid combines with ammonia, forming a compound in which the radical succinyle ($C^4H_4O_2$) replaces two atoms of hydrogen of the ammonia—

$$C^4H_4O_3 + NH_3 = NHC^4H_4O_2 + H_2O.$$

This compound is called succinimide. It dissolves readily in water, and forms beautiful crystals.

Most of the higher terms of the oxalic series are made by the action of dilute nitrate on salts of the adipic series or on oleates.

Hydric sebate is formed by the dry distillation of oleate, but the most ready way of obtaining a sebate in quantity is by heating castor oil soap with potassic hydrate. The soap contains a salt called ricinoleate, and this breaks up with the hydrate into sebate and a volatile alcohol. Hydrated sebacic acid is very slightly soluble in water, and can easily be obtained in crystals.

297. All these salts contain diatomic radicals—oxalyl (C^2O_2), malonyl ($C^3H_2O_2$), succinyl ($C^4H_4O_2$), &c.

These radicals form chlorides corresponding to the hydrates. Thus succinic chloride is $C^4H_4O_2Cl_2$. Oxalates form, however, an exception in this respect, for by the action of phosphoric oxychloride they are broken up into a mixture of carbonic acid and carbonic oxide, whilst hydric chloride and phosphoric hydrate are formed.

These salts are formed on the type of two molecules of water (HOHHOH), the radical replacing two atoms of hydrogen, one in each molecule, whilst imparting to the compounds sufficient acid power to react on two molecules of potassic hydrate, and to neutralize the two atoms of alkali metal in the normal succinates, such as $KO(C^4H_4O_2)OK$.

In this respect the salts of the oxalic series differ from those of the lactic series. For although a lactate contains the diatomic radical lactyl (C^3H_4O) in the place of two atoms of hydrogen of the double molecule (H O H H O H) thus, H O (C^3H_4O) O H, it is only capable of reacting on one atom of potassic hydrate, forming the so-called normal potassic lactate—

H O (C^3H_4O) O K;

and if the second atom of typical hydrogen be expelled by the action of metallic potassium, the compound K O (C^3H_4O) O K is as alkaline as potassium alcohol (K O C^2H_5), and is decomposed even by water like potassium alcohol. The two atoms of typical hydrogen in each molecule of the hydrogen salts of the lactic series are distinguished by the terms 'metallic hydrogen' and 'alcoholic hydrogen.' Metallic hydrogen is that which is easily replaced by metals, and alcoholic hydrogen is that which can only be replaced with difficulty by metals like the typical hydrogen of vinic alcohol.

The difference of acid power in the two series is connected with the fact that each salt of the oxalic series has two atoms of oxygen in its radical, whereas each salt of the lactic series has only one atom of oxygen in its radical. This will be seen if the explicit formulae of glycol, the glycollate, and oxalate, be compared. Glycol is represented thus—

$$\begin{matrix} HOC\ COH \\ H_2\ H_2 \end{matrix}.$$

Neither of its atoms of typical hydrogen is connected with oxidized carbon. If the two atoms of hydrogen united directly with one of the atoms of carbon be replaced by oxygen, the result is the formation of a glycollate—

$$\begin{matrix} HOC\ COH \\ H_2\ O \end{matrix},$$

and if the two atoms of hydrogen united directly with the

other atom of carbon be similarly replaced by oxygen, the oxalate is obtained—

$$\begin{matrix} HOC & COH \\ O & O \end{matrix}$$

In glycol there is no oxidized carbon, and on this account it cannot neutralize even one atom of potassium. In the glycollate there is one atom of oxidized carbon, and the hydrogen united with that atom of carbon by means of oxygen is easily replaced by metals, being 'metallic' hydrogen. The atom of hydrogen connected with the other atom of carbon by means of oxygen is with difficulty replaced by metals, and is 'alcoholic' hydrogen.

In the oxalate there are two atoms of oxidized carbon, and thus both atoms of typical hydrogen are metallic.

298. The chlorides or bromides of divalent radicals react normally upon two molecules of ammonia as upon two molecules of water. Thus ethylenic bromide, heated with ammonia, forms compounds called diamines, derived from two molecules of ammonia ($N_2 H_2 H_2 H_2$), by the replacement of two atoms of hydrogen by one atom of ethylene, forming $N_2 H_2 H_2 (C^2 H_4)$, termed a primary diamine; or by the replacement of four atoms of hydrogen by two atoms of ethylene, forming $N_2 H_2 (C^2 H_4)_2$, a secondary diamine, or by the replacement of the six atoms of hydrogen by three atoms of ethylene, forming $N_2 (C^2 H_4)_3$, a tertiary diamine, called triethylene diamine. Each molecule of these diamines combines with two molecules of hydric chloride, forming salts such as $N_2 H_4 (C^2 H_4) H_2 Cl_2$, and these chlorides, in their turn, unite with platinic chloride, forming double chlorides, such as $N_2 (C^2 H_4)_3 H_2 Cl_2 . Pt Cl_4$.

CHAPTER XLIII.

299. Glycerine has been shewn by the classical investigations of Berthelot to be a triatomic alcohol; and its empirical formula ($C^3 H_8 O_3$) is written on the water-type as containing the trivalent radical glycerile ($C^3 H_5$) in the place of three atoms of hydrogen.

Glycerine is now prepared on a large scale by the distillation of palm oil and other fats in superheated steam. The fat is decomposed, by the action of the steam, into glycerine and hydric palmitate, &c. Thus palmitine, in an excess of steam, takes up three molecules of water—

$$\begin{matrix} C^3 H_5 \\ (C^{16} H_{31} O)_3 \end{matrix} O_3 + 3 H_2 O = \begin{matrix} C^3 H_5 \\ H_3 \end{matrix} O_3 + 3 \begin{matrix} H \\ C^{16} H_{31} O \end{matrix} O.$$

The products are condensed above 100° C; so that the excess of steam passes on, leaving the hydric salts and the glycerine in the condenser. Glycerine is also prepared by the action of litharge in presence of water upon fat. The glycerine can easily be washed away from the plaster which is formed, purified by sulphuretted hydrogen, and evaporated in a water-bath, to drive off the excess of water which is present. In this manner glycerine is obtained, in the form of a thick liquid of sweet but peculiar taste, soluble in water in all proportions, also soluble in alcohol, but insoluble in ether. Glycerine is decomposed at a high temperature, and one of the products formed is acroleine ($C^3 H_4 O$), a volatile liquid of most penetrating odour. Some of the glycerine evaporates in the products of decomposition of the

remainder. Redtenbacher recommends heating glycerine, or a compound of glycerine, with hydro-potassic sulphate, in order to detect it by the odour of acroleine which is formed.

Hydric chloride decomposes glycerine in three successive stages—

$$C^3H_5(OH)_3 + HCl = C^3H_5(OH)_2Cl + H_2O.$$

This first compound is called mono-chlorhydrine. It is in its turn decomposed by hydric chloride, forming dichlorhydrine—

$$C^3H_5(OH)_2Cl + HCl = C^3H_5(OH)Cl_2 + H_2O.$$

The further action of hydric chloride causes the dichlorhydrine to break up into hydric chloride and so-called epichlorhydrine—

$$C^3H_5(OH)Cl_2 = C^3H_5OCl + HCl.$$

Phosphoric chloride, however, forms the normal chlorhydrine—

$$C^3H_5(OH)Cl_2 + PCl_5 = C^3H_5Cl_3 + POCl_3 + HCl.$$

This chlorhydrine is the normal chloride of the trivalent radical glycerile. A corresponding bromide has been obtained; and from the bromhydrine Würtz has reproduced glycerine by the action of argentic acetate, and the subsequent decomposition of the 'acetine' thus obtained.

Other monobasic hydrogen salts act in a similar manner to the chloride. Thus a mixture of hydric sulphate and nitrate transforms glycerine into a heavy oil—glyceric nitrate, or nitrine ($C^3H_5(NO_3)_3$).

By acting upon glycerine by potassium, its typical hydrogen can be partially replaced by the metal, and ethylic iodide replaces this potassium by ethyle.

300. By heating glycerine with a hydrogen salt of the acetic series Berthelot has prepared artificially a considerable number of fats. Thus on the acetate glycerine reacts in three successive proportions—

$$C^3H_8O_3 + C^2H_4O_2 = C^3H_7O_2C^2H_3O_2 + H_2O;$$
$$C^3H_8O_3 + 2\,C^2H_4O_2 = C^3H_6O(C^2H_3O_2)_2 + 2\,H_2O;$$
$$C^3H_8O_3 + 3\,C^2H_4O_2 = C^3H_5(C^2H_3O_2)_3 + 3\,H_2O.$$

These compounds are called monacetine, diacetine, and triacetine. The compounds formed by the action of the higher salts of the series are perfectly analogous to them. In order to separate the fat from the excess of hydrogen salt which was used in the operation, Berthelot acted upon the mixture by sodic carbonate, thereby dissolving out all the salt without decomposing the glycerine compound; and by dissolving the fat in ether he separated it from the free glycerine.

By the action of mono-chlorhydrine on sodic ethylate, monethyl glycerine has been prepared—

$$C^3H_5(OH)_2Cl + Na\,C^2H_5O = Na\,Cl + C^3H_5(OH)_2(OC^2H_5).$$

And in like manner di-chlorhydrine reacts on two molecules of sodic ethylate, forming di-ethylic glycerine; and the triethyline has been obtained by the action of ethylic iodide on di-ethyl-sodic glycerine—

$$C^3H_5(ONa)(OC^2H_5)_2 + C^2H_5I = NaI + C^3H_5(OC^2H_5)_3.$$

301. By the oxidation of glycerine, a hydrogen salt called glycerate, of the composition $C^3H_6O_4$, has been obtained.

Glycerate contains the trivalent radical C^3H_3O; but it appears to be monobasic, so that two of the typical atoms of hydrogen in it are considered as alcoholic hydrogen, while one only is metallic $C^3H_3O.H_2O_2(OH)$.

A hydrogen salt, called tartronate, has been obtained by the decomposition of nitro-tartrate. The tartronate has the composition $C^3H_4O_5$; and Kekulé suggests that it may be the next product of the oxidation of glycerine, so that its rational formula would then be $C^3HO_2H_2O_2(OH)$.

Another class of salts, nearly related to these, are the malates such as $(C^4H_6O_5)$; these salts occur in goose-

berries, rhubarb, sour apples, barberries, and many other vegetables; but they are most conveniently prepared from the juice of unripe mountain-ash berries.

Malates are dibasic; but, as Kekulé suggests, its radical is probably trivalent, according to the formula $C^4H_3O_2 . H_2O_2$ (OH), according to which it is represented as homologous with tartronate, and is derived from butylic glycerine $C^4H_7(OH)_3$.

Calcic malate ($Ca\,C^4H_4O_5$) is insoluble in water. It dissolves in dilute hydric nitrate; and the double salt

$$H_2Ca(C^4H_4O_5)_2$$

crystallizes out easily from this solution.

Plumbic malate becomes semi-fluid and crystalline by heating in a solution of plumbic acetate.

Hydric iodide reduces malate to succinate—

$$C^4H_6O_5 + 2\,HI = C^4H_6O_4 + H_2O + I^2.$$

Malates rotate a polarized ray of light.

By the action of heat the malate yields two hydrogen salts isomeric with one another, and differing from it by containing the elements H_2O less than the malate in each molecule—

$$C^4H_6O_5 - H_2O = C^4H_4O_4.$$

These salts are called maleate and fumarate. They combine with nascent hydrogen, forming succinate—

$$C^4H_4O_4 + H^2 = C^4H_6O_4.$$

Many vegetables contain a nitrogenized crystallizable compound called asparagine, which is represented by the formula $C^4H_4O_3(NH_2)_2$. Asparagine behaves as the malic amide. By prolonged contact with hot water, it is converted into ammonic malamate—

$$C^4H_4O_3(NH_2)_2 + H_2O = NH_4C^4H_4O_4NH_2.$$

By the action of nitrous acid it is decomposed, yielding a kind of malate, which does not rotate light—

$$C^4H_4O_3(NH_2)_2 + N_2O_3 = C^4H_6O_5 + 2\,N^2 + H_2O.$$

302. By the dry distillation of glycerine, a volatile body of very pungent odour, called acrolein, is formed. It has the composition $C^3 H_4 O$, being formed from a molecule of glycerine by the loss of the elements of two molecules of water. It is analogous to the aldehydes in its properties, and is often termed acrylic aldehyde. By its oxidation, hydric acrylate ($C^3 H_4 O_2$) is formed. This body belongs to a series of monobasic salts, called the acrylic series, the members of which contain two atoms of hydrogen in each molecule less than the corresponding salts of the acetic series. The next term of this series is the crotonate ($C^4 H_6 O_2$), which has been extracted from the croton-seed oil.

Hydric angelate ($C^5 H_8 O_2$) is obtained from angelica root. The other terms of this series are—

The Pyroterebate.. $C^6 H_{10} O_2$,	The Hypogeate ... $C^{16} H_{30} O_2$,
„ Damalurate .. $C^7 H_{12} O_2$,	„ Oleate ..... $C^{18} H_{34} O_2$,
„ Campholate .. $C^{10} H_{18} O_2$,	„ Brassate ..... $C^{22} H_{42} O_2$.
„ Moringate ... $C^{15} H_{28} O_2$,	

303. Oleates are an exceedingly common accompaniment of the compounds of the acetic series. The glycerine derivative of oleic acid, called oleine, is liquid and uncrystallizable, whereas stearic and palmitic acid, &c. form, with glycerine, compounds called stearine and palmitine, which are solid at the ordinary atmospheric temperature, and which crystallize out from their solution in oleine on cooling. Thus olive oil in cold weather deposits crystals of palmitine, &c., while oleine remains fluid and can be pressed out from the crystals. Alkaline oleates are not decomposed by dilution with water, as stearates, &c. are; and by neutralizing the alkali liberated by the dilution of a concentrated solution of a stearate, and then diluting again, some more stearate is decomposed, and it is stated that the whole of the alkaline stearate can be decomposed in a mixture with an

oleate, by a frequent repetition of this process. Oleine is more soluble in ether than stearine or palmitine, and can in great part be separated from the solid fats by washing with ether.

Plumbic oleate is readily soluble in ether, whereas plumbic palmitate or stearate, &c. are nearly insoluble.

Hydric oleate is represented by the formula $C^{18}H_{34}O_2$.

A mixture of lead salts of the fatty acids is used; it is named plaster. Olive oil is frequently used for the preparation of plaster. Litharge in presence of water gradually decomposes it at 100°, forming glycerine.

Many oils—such as those expressed from the seeds of lint, poppy, walnut, hemp, ricinus, or castor-oil plant—possess the property of becoming thick, and ultimately hard and resinous, by exposure to the air. This process takes place still more rapidly if the oil has been heated with litharge. These so-called 'drying' oils are used by painters to fix their colours. Linseed oil and poppy oil appear to be derivatives of a salt of the composition $C^{16}H_{28}O_2$, to the oxidation of which this 'drying' process is due.

CHAPTER XLIV.

304. Tetratomic compounds are chiefly known among acids, but a crystallizable body called erithrite has been extracted from various lichens, and Berthelot has proved that it reacts upon hydric salts under similar circumstances to glycerine. The formula of erithrite is $C^4H_{10}O_4$, and it is considered as a tetratomic alcohol of the formula $C^4H_6(OH)_4$.

Hydric iodide decomposes it, with formation of a compound isomeric with butylic iodide (C^4H_9I).

Hydric Tartrate ($C^4H_6O_6$) is classed by Kekulé as a tetratomic compound, and thus related to erithrite by replacement of four atoms of hydrogen in the radical C^4H_6 by two atoms of oxygen ($C^4H_2O_2(OH)_4$).

Tartrates are contained in many vegetable juices. The hydrogen salt is usually prepared from argol, the crude hydro-potassic tartrate which collects from acid continental wines in the form of a reddish crust. The salt is decomposed by boiling with chalk, forming a precipitate of calcic tartrate and a solution of potassic tartrate—

$$2\,C^4H_5KO_6 + CaCO_3 = C^4H_4CaO_6 + C^4H_4K_2O_6 + CO_2 + H_2O.$$

The solution of the potassic salt is transformed into calcic tartrate by the action of calcic chloride—

$$C^4H_4K_2O_6 + CaCl_2 = C^4H_4CaO_6 + 2\,KCl.$$

The two portions of calcic salt obtained by these operations are decomposed by dilute hydric sulphate, and the tartrate is usually evaporated in vacuum pans.

It is thus obtained in the form of clear crystals, which contain no water of crystallization. When heated these crystals become electrical, shewing two opposite electrical charges at two opposite corners. These polarities are reversed during the process of cooling.

The tartrate dissolves readily in water, and its solution has a powerfully acid reaction. It is very liable to become mouldy, and to decompose on keeping. The aqueous solution of tartrates is dextrorotatory.

If present in sufficient quantity with a salt of a heavy metal, a tartrate prevents the precipitation of the metallic oxide by potash. Alkaline solutions thus formed allow the heavy metal to be precipitated by sulphuretted hydrogen. This property is, however, not by any means characteristic of tartrates, as it belongs equally to many other polybasic salts.

305. Tartrates are decomposed by heat, and the odour of the products of their destructive distillation possesses some resemblance to that of burnt sugar, and is employed occasionally as a means of recognizing the hydrogen salt.

When the salt is cautiously heated it loses a molecule of water, forming tartaric acid—

$$C^4H_6O_6 - H_2O = C^4H_4O_5;$$

and this acid is capable of combining with the hydrate, forming the so-called ditartrate. Among the products of the dry distillation of tartrate are pyruvate ($C^4H_4O_3$), and pyrotartrate ($C^5H_8O_4$). It is easy to account for the formation of these salts. Thus:

$$C^4H_6O_6 - CO_2 - H_2O = C^3H_4O_3, \text{ and}$$
$$2\,C^3H_4O_3 - CO_2 = C^5H_8O_4.$$

Acetate accompanies these products.

When fused with potassic hydrate tartrates break up into an acetate and an oxalate—

$$C^4H_4K_2O_6 + KHO = C^2H_3KO_2 + C^2K_2O_4 + H_2O.$$

Tartrates are amongst the best characterized dibasic salts. When half neutralized by potash the hydric salt forms the slightly soluble hydro-potassic tartrate commonly called cream-of-tartar. But when twice as much potash is added, the salt is dissolved, with formation of the readily soluble normal tartrate—

$$C^4 H_4 K_2 O_6.$$

When lime-water is added gradually to a solution of the hydrogen salt, no precipitate is produced so long as the liquid is acid, but as soon as it becomes neutral a white precipitate of normal calcic tartrate is formed. This salt dissolves in cold potash, but is precipitated by boiling. It dissolves also in ammonic chloride.

Sodium forms a normal tartrate and a double tartrate with hydrogen. This hydro-sodic tartrate is an exceedingly convenient reagent for the distinction of potassium and sodium in their salts, as it precipitates concentrated solutions of potassic salts and has no action on sodic salts.

Rochelle salt is the name given to sodio-potassic tartrate, a salt which crystallizes in singularly well-formed crystals.

Tartrates are readily oxidized by hydric nitrate. They reduce metallic silver from solutions of its salts. One of the commonest tartrates is the so-called tartar-emetic, potassio-antimonic oxytartrate ($C^4 H_4 K Sb O_7$). This salt is usually prepared by boiling pure antimonic oxide with hydro-potassic tartrate. It may be considered as containing the monovalent radical Sb O in place of one atom of potassium of the normal tartrate—

$$C^4 H_4 K (Sb O) O_6.$$

306. The racemate is isomeric with common tartrate. It has no rotating action on a polarized ray of light. Its solution causes a precipitate when added to a solution of calcic chloride, and the racemate is thus distinguished from the

tartrate. Pasteur has shewn that the racemate is a compound of tartrate (dextrorotatory) with an isomeric body which he calls levorotatory tartrate. The two are separated by crystallizing a solution of ammonio-sodic racemate. Two varieties of crystals are formed, each of them hemihedral, but one having the opposite modifications to the other; so that if a model of one of the crystals were made of cardboard it would represent the other variety when turned inside out.

Tartrate and racemate are formed by the cautious oxidation of saccharate and mucate by hydric nitrate. They are, in their turn, easily oxidized by the nitrate, forming oxalate, and ultimately carbonic acid. Tartrates also reduce metallic silver from solutions of its salts.

The tartrate has been made from succinate. The first step of the process is to form the so-called dibromo-succinate, $C^4H_4Br_2O_4$. The silver-salt of this body is next prepared by precipitation. When boiled for some time in contact with water this silver salt takes up the elements of two molecules of water, giving up in their place its bromine and silver together as argentic bromide—

$$C^4H_2Br_2Ag_2O_4 + 2\,H_2O = 2\,BrAg + C^4H_6O_6.$$

Homotartrate is the name given by its discoverer, Kekulé, to a salt of the composition $C^5H_8O_6$, formed by the action of argentic hydrate on the compound of bromine with itaconate. This compound is homologous with dibromo-succinate, and is called dibromopyro-tartrate—

$$C^5H_6Br_2O_4 + 2\,AgHO = 2\,AgBr + C^5H_8O_6.$$

307. The **Citrate** ($C^6H_8O_7$) is usually prepared from lemon-juice. It is also contained in tamarinds, and in many other acid fruits.

The expressed juice is neutralized by lime, and the dry calcic citrate is imported into this country for the preparation

of the hydric salt. The salt is prepared from this calcic salt by the action of hydric sulphate, very much in the same way as the tartrate.

The salt crystallizes readily from water, and the crystals contain a molecule of water of crystallization.

Citrates are tribasic, and the formula of the hydric salt is written on the water-type as containing the trivalent radical C^6H_4O: thus, $C_6H_4O_3(HO)(HO)_3$. It is thus considered to contain four atoms of typical hydrogen, three of which are metallic and replaceable by potassium, sodium, &c., while the fourth is alcoholic hydrogen.

Potassic Citrate ($K_3C^6H_5O_7$), as well as hydro-di-potassic citrate ($HK_2C^6H_5O_7$) and di-hydro-potassic citrate ($H_2KC^6H_5O_7$), are readily soluble in water; and the citrate can be distinguished from the tartrate by the non-precipitation of potash by an excess of hydric citrate.

When lime-water is added gradually to an aqueous solution of hydric citrate, a double salt is at first formed; but even when the salt is neutralized by the formation of the normal salt $Ca_3(C^6H_5O_7)_2$, no precipitate is formed in the cold. On boiling an alkaline mixture of citrate and lime-water, the salt is precipitated.

When the citrate is cautiously heated, it loses the elements of a molecule of water, forming aconitate ($C^6H_6O_6$); and when aconitate is heated to a still higher temperature than that at which it was formed, carbonic acid is given off, and a salt of the composition $C^5H^6O_4$ is formed. This salt is called itaconate. The citraconate, isomeric with itaconate, is formed at the same time, and a third isomeric body is called mesaconate.

Pentatomic compounds are as yet but little known. Kekulé places, however, in this group two hydric salts — aposorbate ($C^5H_8O_7$), a dibasic salt supposed to contain the pentavalent radical $C^5H_8O_2$. It was made by Des-

saignes, by the action of hydric nitrate on sorbin. The other pentatomic salt is desoxalate ($C^5H_6O_8$), obtained by Löwig among the products of the action of sodium on oxalic ether. Desoxalates are supposed to contain the radical C^5HO_3, and they are tribasic. The hydric desoxalate breaks up when heated into carbonic acid and racemate—

$$C^5H_6O_8 = C^4H_6O_6 + CO_2.$$

308. Mannite ($C^6H_{14}O_6$) is a hexatomic alcohol, containing the radical C^6H_8 in the place of six atoms of hydrogen in six molecules of water ($C^6H_8(OH)_6$).

It is contained in manna, and is frequently formed from sugar by a process of fermentation. It has been made by the action of nascent hydrogen, evolved by sodium amalgam, on uncrystallizable sugar. It is readily soluble in water, but far less soluble in alcohol. It melts between 160° and 165°, and boils, with partial decomposition, at 200°.

Mannite reduces gold and silver from aqueous solutions of their salts, but it does not reduce copper from cupric oxide in presence of free potash.

It reacts with hydric stearate, &c., in the same sort of way as glycerine, and Berthelot has obtained mannitic tetra-hydric di-stearate and mannitic di-hydric tetra-stearate.

Mannitic nitrate ($C^6H_8(NO_3)_6$) is formed by the action of a mixture of strong nitrate and sulphate upon mannite. Sulphuretted hydrogen in presence of alcohol and ammonia reduces it to mannite. Hydric iodide decomposes mannite, forming a compound isomeric with caproic iodide ($C^6H_{13}I$).

Mannitan ($C^6H_{12}O_5$) is formed by the removal of a molecule of water from mannite, by the action of heat.

Mannide ($C^6H_{10}O_4$) has been obtained by Berthelot by heating mannite to 200° or 250° with hydric butyrate.

Hydric mannitate ($C^6H_6O(OH)_6$) is formed by the action of air on a mixture of platinum black and moist mannite. It is probably monobasic.

309. Hydric Saccharate and **Mucate** ($C^6H_4O_2(OH)_6$) are formed by the action of dilute hydric nitrate on mannite. Saccharate is also formed by the first action of the nitrate on several kinds of sugar. It is most easily prepared from common cane-sugar. One part by weight of sugar is heated with three parts by weight of nitrate, of density 1.25, and removed from the fire as soon as the action is fairly started. After the liquid has cooled down to about 50° it is kept at this temperature as long as any fumes are evolved. It is then diluted with half its volume of water, and half neutralized by potash. When allowed to stand for some days the liquid deposits crystals of hydro-potassic saccharate—

$$C^6H_4O_2(OH)_4(OH)(OK).$$

Its normal potassic salt has the composition $C^6H_4O_2(OH)_4(OK)_2$. Hydric saccharate has not been obtained in the crystalline state. When made from cane-sugar it is dextrorotatory. By the gentle action of hydric nitrate it forms dextrotartrate.

There are two saccharic ethers corresponding to the potassium salts above named, and an amide corresponding to the normal ether and obtained from it by the action of ammonia—

$$\begin{matrix} C^6H_4O_2 \\ H_4(C^2H_5)_2 \end{matrix} O_6 + 2NH_3 = \begin{matrix} C^6H_4O_2 \\ H_4(NH_2)_2 \end{matrix} O_4 + 2\,C^2H_5^{\,H}O.$$

Mucate, isomeric with saccharate, is formed by the action of nitrate on milk-sugar, or gum-arabic. According to Pasteur it is best made from galactose.

Hydric mucate is easily deposited in the crystalline form from its aqueous solution, for it is very slightly soluble in

cold water. Like saccharates it is dibasic. On dry distillation it yields pyromucate—

$$C^6 H_{10} O_8 = C^5 H_4 O_3 + 3 H_2 O + C O_2.$$

Hydric iodide reduces mucates, and, according to Crum-Brown, it appears that adipate is formed by the reduction—

$$C^6 H_{10} O_8 + 8 H I = C^6 H_{10} O_4 + 4 H_2 O + 4 I^2.$$

Hydric nitrate oxidizes a mucate, with formation of racemate; and this, in its turn, is subsequently oxidized to oxalate.

CHAPTER XLV.

310. One of the most important families of organic bodies is that of the so-called carbonic hydrates; including sugars, gums, starch, woody fibre, &c. These bodies contain oxygen and hydrogen in the proportions in which those elements form water; or, in other words, they contain twice as many atoms of hydrogen as of oxygen, but it is by no means probable that these elements are combined with one another in the form of water. They are probably related to alcohols in their composition, containing polyvalent radicals, such as $C^6 H_6$, in lieu of the hydrogen of water.

These compounds are classified by Kekulé under the three following formulæ, viz.—

$$C^6 H_{12} O_6;$$
$$C^{12} H_{22} O_{11};$$
$$C^6 H_{10} O_5.$$

It may be, however, that some of them ought to be represented by multiples of these formulæ.

Grape-sugar, or dextrose, and uncrystallizable sugar, are two of the most important compounds, having the formula $C^6 H_{12} O_6$. Galactose is also isomeric with them, and, like them, is capable of undergoing alcoholic fermentation under the action of yeast. These fermentable sugars are formed by the action of hydric salts on compounds belonging to the other families of carbonic hydrates. Thus dextrose is formed by boiling starch or dextrine with dilute sulphate. It is also formed together with levulose by the action of dilute

sulphate on cane-sugar. Levulose is alone formed from inulin. And galactose is formed from milk-sugar by the action of dilute hydric salts. These sugars are also formed from the same materials by the action of yeast. Thus cane-sugar in a fermenting fluid takes up the elements of water, and forms a molecule of dextrose and a molecule of levulose. Dextrose is best obtained from so-called candied honey, i. e. honey which has deposited crystals by long standing. The syrup is drained from these crystals by allowing them to lie on a porous tile. They are then dissolved by the aid of heat in spirits of wine, and crystallized.

Dextrose dissolves in about an equal weight of water, and its solution is not decomposed by dilute sulphate. It reduces ferric salts to ferrous salts, and reduces metallic silver from many of its solutions. It dissolves cupric hydrate in presence of caustic potash, and the solution deposits cuprous hydrate when gently heated. A lime compound is obtained by dissolving calcic hydrate in a solution of dextrose, and then adding alcohol. Its composition is represented by the formula—

$$C^6 H_{10} Ca O_6 H_2 O.$$

Dextrose also combines with common salt. There are three crystallizable compounds, but the one most easily obtained consists of two molecules of dextrose combined with one molecule of salt and one of water—

$$(C^6 H_{12} O_6)_2 Na Cl H_2 O.$$

311. Compounds of glucose with acids are called **Glucosates.** Many of them, such as tannin, amygdalin, salicin, &c., occur in the vegetable kingdom.

These bodies are decomposed in a manner which may be compared to the decomposition of fats by water. Thus, when boiled with a dilute mineral hydric salt, tannin takes

up the elements of water, and decomposes into glucose and hydric gallate—

$$\underbrace{C^{27}H_{22}O^{17}}_{\text{Tannin.}} + 4\,H_2O = 3\underbrace{C^7H_6O_5}_{\text{Gallate.}} + \underbrace{C^6H_{12}O_6}_{\text{Glucose.}}.$$

In like manner salicin breaks up into saligenine and glucose—

$$\underbrace{C^{13}H_{18}O_7}_{\text{Salicin.}} + H_2O = \underbrace{C^7H_8O_2}_{\text{Saligenine.}} + \underbrace{C^6H_{12}O_6}_{\text{Glucose.}}.$$

The decomposition of amygdaline is more complicated. It takes place in presence of certain ferments, forming benzoic aldehyde, prussic acid, and glucose—

$$C^{20}H_{27}NO_{11} + 2\,H_2O = C^7H_6O + CNH + 2\,C^6H_{12}O_6.$$

Berthelot has prepared several glucosates by heating glucose with hydrated organic hydric salts. Acetic glucosate was obtained by heating glucose for about 50 hours to 100° with the acetate. It contains six atoms of acetyl, thus—($C^6H_4(C^2H_3O)_6O_5$), and the glucose lost a molecule of water at the same time, forming glucosan ($C^6H_{10}O_5$), of which, properly speaking, this compound is the acetate. Similar compounds have been obtained with butyrate and stearate, containing in one molecule two atoms of the radicals of these salts.

Levulose is not easily obtained in a state of purity, as dextrose, which usually accompanies it in sweet fruits, can only be separated approximatively from it by alcohol. In contact with nascent hydrogen, evolved by sodium, levulose takes up hydrogen and is converted into mannite, a property which dextrose does not seem to possess—

$$\underbrace{C^6H_{12}O_6}_{\text{Levulose.}} + H^2 = \underbrace{C^6H_{14}O_6}_{\text{Mannite.}}.$$

It is less rapidly decomposed by yeast than dextrose;

and accordingly a mixture of the two, such as is formed by boiling common sugar with dilute sulphate, becomes more and more levorotatory up to a certain point, in proportion as the dextrose is broken up.

Its compound with lime is less soluble in water than the compound containing dextrose.

In order to separate levulose from dextrose, Dubrunfaut recommends that 10 parts of so-called **inverted sugar** be mixed with 6 parts of calcic hydrate and 100 of water. After the mixture has been shaken for some time a deposit is formed, containing levulose combined with lime. Hydric oxalate liberates the levulose from this compound.

Galactose is obtained by boiling milk-sugar with very dilute sulphate. It has much resemblance to glucose, but, unlike glucose, it does not combine with salt.

312. Sugar ($C^{12}H_{22}O_{11}$), called by way of distinction cane-sugar, is found in the juices of many plants. It is mostly prepared from the juice of the sugar-cane, but in many parts of the continent of Europe it is prepared from beet-root. The manufacture of sugar from the sugar-cane is divided into two distinct operations: first, the preparation of a crude sugar in the neighbourhood in which the sugar is grown; and, secondly, the purification of the crude sugar by the so-called process of refining—an operation which is only performed with advantage in or near some large town, where skilled labour is abundant.

The freshly-cut sugar-canes are first passed through rollers, which press out the greater part of the juice; and this juice is rapidly evaporated down after the neutralization of its acidity by lime. The mother-liquid drained off from the crystals of sugar is known by the name of molasses, or treacle.

The **refining of sugar** is effected by dissolving it in water, and depriving it of its colouring matter by animal

charcoal and albumen (from ox blood). The solution is evaporated in a so-called vacuum pan—a large boiler in which the syrup is boiled down—by the aid of a partial vacuum maintained by a powerful air-pump and condenser. The lower temperature at which ebullition thus takes place, saves the sugar from the partial decomposition which it would undergo if boiled for an equal length of time under the atmospheric pressure.

When allowed to crystallize slowly, sugar is obtained in the form of very hard and regular crystals, which are known by the name of sugar-candy. For most purposes the consumers prefer to use sugar in very small crystals, and to obtain it in that form. The concentrated syrup is agitated artificially during the process of crystallization. A thick magma is thus obtained, which is poured into moulds, where the little crystals are cemented together by the deposition of more sugar between them, and assume the form of a sugar-loaf.

Sugar has a density of 1.6. It dissolves in about one-third of its weight of cold water, and in still less hot water, and the solution is dextrorotatory. It is not soluble in ether or in cold alcohol. It melts at 160°, and becomes coloured when heated to a higher temperature. It is completely destroyed by dry distillation.

313. Dilute mineral hydric salts transform sugar, with assimilation of water, into a mixture of dextrose and levulose. This mixture is called inverted sugar. Yeast effects the same transformation, and these products necessarily precede the formation of alcohol and the other products of vinous fermentation.

Sugar holds cupric oxide in solution in presence of caustic potash, and cuprous oxide is deposited very slowly indeed from this solution on the application of heat. When heated with dilute hydric nitrate it forms saccharate, tartrate,

and oxalate. Caustic potash has very little action on sugar even at 100°, and serves to distinguish it from dextrose and levulose.

A solution of sugar is precipitated by baryta, the compound $C^{12}H_{22}O_{11}BaO$ being formed.

Lime dissolves very freely in syrup, forming various compounds.

The compound $C^{12}H_{22}O_{11}CaO$ is obtained by dissolving lime in aqueous solutions of sugar, taking care to keep the sugar in slight excess, and then adding alcohol to the solution. The compound is thus precipitated.

$C^{12}H_{22}O_{11}Ca_2O_2$ is obtained by saturating a solution of sugar and lime, by digesting it with an excess of the base, and then precipitating the filtered liquid by alcohol.

$C^{12}H_{22}O_{11}Ca_3O_3$ is precipitated by boiling an aqueous solution of sugar previously saturated with lime.

Milk-Sugar ($C^{12}H_{22}O_{11}$) is obtained by evaporating to crystallization the clear liquid called whey, obtained by allowing skimmed milk to remain in contact with rennet until all the casein is deposited from it. The crystals first obtained can be purified by the action of animal charcoal, and recrystallization. When dried at 100° milk-sugar contains a molecule of water of crystallization, which can be expelled at 140°C. The crystals $C^{12}H_{22}O_{11}H_2O$ require about six times their weight of cold water for their solution; but they dissolve in twice their weight of boiling water. They are remarkably insipid; but the aqueous solution has a very sweet taste. It is dextrorotatory.

Dilute mineral hydric salts convert milk-sugar into galactose, and yeast probably effects the same transformation before alcoholic fermentation sets in.

Cheese transforms milk-sugar into a lactate, alcohol and

carbonic acid being formed in small quantity at the same time.

Milk-sugar holds cupric oxide in solution in presence of potash; and the solution readily deposits cuprous oxide even in the cold.

Dilute hydric nitrate oxidizes milk-sugar, with formation of mucate.

CHAPTER XLVI.

314. Dextrine ($(C^6 H_{10} O_5)_n$) is a neutral and insipid body, used in the impure state under the name of British gum. It is obtained by heating starch to about 160°. The starch is sometimes moistened with exceedingly dilute nitrate before heating. Dextrine is also formed from starch by the action of certain ferments. It is named from its powerfully dextrorotatory action on light. It dissolves in water, but not in alcohol or ether. It does not reduce cupric oxide when boiled with it in an alkaline liquid. Dilute hydric salts transform dextrine into dextrose. The nitrate does not form mucate on oxidizing it.

Gum-Arabic, or tree-gum, has the same empirical compound as dextrine. Its aqueous solution is levorotatory. Moderately strong nitrate oxidizes gum-arabic, with formation of the mucate.

Other members of this same natural family are—

Lichenine, which is extracted by boiling water from Iceland moss. Its solution gelatinizes on cooling.

Inuline, prepared from dahlia-roots.

Glycogen, discovered by Bernard in the liver.

Starch ($(C^6 H_{10} O_5)_n$) is contained in many vegetables, in the form of granules varying in size according to the vegetable from which it is obtained. Thus the granules of potato-starch have a diameter of nearly 0.2 millimetre, whilst those from Indian-corn have only a diameter of 0.03, and those from the seed of chenopodium quinoa have a diameter of about 0.002.

Starch is usually prepared from potatoes or rice. The granules are washed out from the fibrous substances in which they are interspersed, and they collect at the bottom of vessels in which the water is allowed to stand. Dilute caustic soda is used to dissolve out from the starch the albuminous matter with which it is at first mixed, and which would cause its decomposition if left in it.

Starch is not, properly speaking, soluble in water; but when it is heated to about 80° with water, the granules swell up and burst, forming a paste. When long boiled in water starch passes over into a soluble substance usually called **soluble starch**. This soluble compound is exceedingly dextrorotatory. It is precipitated by alcohol in the form of a white powder, but retains its solubility in water.

Granulous starch and soluble starch are characterized by the deep blue colour of the compound which each of them forms with iodine.

Starch granules are dissolved by caustic potash, forming a liquid which has no rotatory action on a ray of light.

Dilute hydric salts, as well as diastase, and some other ferments, dissolve starch by transforming it into a mixture of dextrine and dextrose. Starch is not dissolved by ammonic cuprate.

315. Cellulose, or **Woody fibre** ($(C^6H_{10}O_5)_n$), is the name usually given to the most insoluble bodies of this class. They are not soluble in water, nor in dilute caustic potash. Ammonic cuprate dissolves woody fibre. The material is most easily obtained in a state of purity from fresh and picked cotton-fibre. Caustic potash, alcohol, and ether are used successively to dissolve out foreign substances adhering to the fibres; and they are then very carefully washed and dried. Woody fibre immersed for some time in a concentrated solution of potash appears to combine with the

alkali, and to form a compound containing two atoms of potassium to twenty-four atoms of carbon—

$$C^{24} H_{40} O_{20} K_2 O.$$

Water dissolves out all the potash from this compound, reproducing woody fibre. Strong hydric sulphate reacts on cellulose, forming a conjugated compound, analogous to sulphovinic acid.

When paper is immersed for a short time in a mixture of two volumes oil of vitriol and one of water, and thoroughly cleansed by repeated washings with water, and ultimately with ammonia, it is changed into a substance possessing considerable resemblance to parchment, and usually called **'vegetable parchment.'** Strong hydric nitrate reacts on woody fibre, forming products of substitution of $N O_2$ for hydrogen in the cotton. A mixture of strong nitrate and sulphate replaces three atoms of hydrogen by $(N O_2)_3$ in the group $C^6 H_{10} O_5$, and the compound $C^6 H_7 (N O_2)_3 O_5$ is the valuable explosive material called **gun-cotton.** A variety of nitrocellulose containing a smaller proportion of the radical $N O_2$ is used for the preparation of **collodion**, which is a solution of it in ether and a little alcohol. The gun-cotton ($C^6 H_7 (N O_2)_3 O_5$) does not dissolve in ether and alcohol, but it dissolves in acetic ether. An alcoholic solution of potassic sulph-hydrate decomposes these bodies, reproducing woody fibre from all of them.

Strong hydric sulphate dissolves cellulose, transforming it into a substance analogous to starch, insoluble in water, but swelling up by contact with it, and becoming blue when placed in contact with iodine. By longer action of the sulphate a substance very much like dextrine is formed. When this dextrine from woody fibre is boiled with dilute sulphate it is converted into dextrose.

CHAPTER XLVII.

316. Hydric Urate ($C^5H_4N_4O_3$) is in its constitution related to urea. It occurs sometimes in human urine, and if present in considerable quantity gives rise to the formation of concretions in the bladder and in other organs.

It is most easily obtained in a pure state from the urine of the boa-constrictor or other large serpents. This substance resembles chalk in its appearance, and consists chiefly of ammonic urate. Dilute caustic potash dissolves it at a boiling heat, evolving ammonia. The solution contains potassic urate, $C^5H_2N_4O_3K_2$—a salt of exceedingly alkaline properties. There is in the solution some colouring matter, which is most easily separated from the compound by passing carbonic acid through the impure solution of the potash salt. A double salt is thus precipitated (hydro-potassic urate $C^5H_2N_4O_3HK$), while the colouring matter remains mostly dissolved in the alkaline carbonate. By repeatedly dissolving in potash and reprecipitating by carbonic acid a colourless urate is at last obtained, from which the urate is precipitated in the form of a white crystalline powder by dilute hydric chloride or sulphate.

Hydric urate requires about 18,000 parts of cold water for its solution. It is insoluble in alcohol and ether.

On dry distillation it is entirely decomposed, forming amongst other products cyanurate, urea, ammonic cyanide, &c.

Its potassic salts are more soluble in water than its sodic

salts, and lithia dissolves it even more freely than potash. Its derivatives with the alkaline earths and the heavy metallic oxides are nearly insoluble in water. Urates are detected by the bright red colour which is formed when crystals of hydric urate are moistened with the nitrate, dried by the aid of gentle heat, and then moistened with ammonia. The reaction is due to the formation of murexide.

Another way of detecting urates, described by Schiff, is to dissolve the urates in sodic carbonate and drop the solution on to paper moistened by silver nitrate. A brown colour is produced, owing to the reduction of silver.

317. The derivatives obtained from the urates by the action of various reagents are exceedingly numerous. A few only of them can be here mentioned.

Alloxan ($C^4H_2N_2O_4$) is formed by the action of various oxidizing agents, such as hydric nitrate or chlorate. Urea is formed at the same time thus—

$$\underbrace{C^5H_4N_4O_3}_{\text{Hydric urate.}} + O + H_2O = \underbrace{C^4H_2N_2O_4}_{\text{Alloxan.}} + \underbrace{CH_4N_2O.}_{\text{Urea.}}$$

Alloxanates ($C^4H_4N_2O_5$), such as the hydric salt, are formed by the action of bases on alloxan. The baric salt ($C^4H_2BaN_2O_5$) is decomposed by boiling into urea and baric mesoxalate—

$$\underbrace{C^4H_2BaN_2O_5}_{\text{Baric alloxanate.}} + H_2O = \underbrace{C^3BaO_5}_{\text{Baric mesoxalate.}} + \underbrace{CH_4N_2O.}_{\text{Urea.}}$$

Alloxantin ($C^8H_4N_4O_7$) is formed by the action of reducing agents, such as sulphuretted hydrogen, sulphurous acid, &c. on alloxan—

$$\underbrace{(C^4H_2N_2O_4)_2}_{\text{Alloxan.}} + H^2 = \underbrace{C^8H_4N_4O_7}_{\text{Alloxantin.}} + H_2O.$$

Hydric Dialurate ($C^4H_4N_2O_4$) is formed by the further action of reducing agents with the aid of heat—

$$\underbrace{C^4H_2N_2O_4}_{\text{Alloxan.}} + H^2 = \underbrace{C^4H_4N_2O_4}_{\text{Dialurate.}}.$$

Hydric Parabanate ($C^3H_2N_2O_3$) is formed by the action of oxidizing agents, such as nitrate, on alloxan—

$$\underbrace{C^4H_2N_2O_4}_{\text{Alloxan.}} + O = \underbrace{C^3H_2N_2O_3}_{\text{Parabanate.}} + CO_2.$$

Parabanates undergo decompositions analogous to those of alloxan, and hydric parabanate may be considered as a kind of alloxan containing the elements CO less than alloxan itself. Thus—

Hydric Oxalurate ($C^3H_4N_2O_4$) is obtained by the action of a base on the parabanate. And oxalurates decompose when boiled into urea and corresponding oxalates.

The formation of oxalurates from parabanates is similar to that of alloxanates from alloxan. Oxalurate differs from alloxanate in composition by the elements CO. When boiled with a hydric salt a solution of parabanic acid decomposes into oxalate and urea—

$$C^3H_2N_2O_3 + 2\,H_2O = C^2H_2O_4 + CH_4N_2O;$$

oxalurate being no doubt first formed.

The two salts yield urea, while alloxanate yields a mesoxalate (C^3O_5Ba), and oxalurate yields an oxalate (C^2O_4Ba); and the mesoxalate has the same CO beyond the elements of the oxalate which alloxanate has beyond the elements of the oxalurate.

318. Mesoxalates and **Oxalates** may with advantage be compared to carbonates, as an oxalate contains CO in addition to the elements of a carbonate. Thus—

CO_3H_2	$C^2O_4H_2$	$C^3O_5H_2$
Carbonate.	Oxalate.	Mesoxalate.

If we represent these salts on the type of two molecules of water $\left(\begin{matrix}H_2\\H_2\end{matrix}O_2\right)$ we have the series $\begin{matrix}CO\\H_2\end{matrix}O_2$, $\begin{matrix}C^2O_2\\H_2\end{matrix}O_2$, $\begin{matrix}C^3O_3\\H_2\end{matrix}O_2$; containing the radicals CO (carbonyl), C^2O_2 (oxalyl), and C^3O_3 (mesoxalyl). If, as Kekulé has suggested, the carbonate be represented as derived from methylenic glycol $\left(\begin{matrix}CH_2\\H_2\end{matrix}O_2\right)$ by the replacement of H^2 by O, while glycollate in like manner is derived from ethylenic glycol $\left(\begin{matrix}C^2H_4\\H_2\end{matrix}O_2\right)$ by the same substitution, and oxalate by the replacement of the four atoms of hydrogen in the glycol by two atoms of oxygen, then the mesoxalate will be derived from propylenic glycol $\left(\begin{matrix}C^3H_6\\H_2\end{matrix}O_2\right)$ by the replacement of the six atoms of hydrogen in the radical by three atoms of oxygen, the lactate $\left(\begin{matrix}C^3H_4O\\H_2\end{matrix}O_2\right)$ and malonate $\left(\begin{matrix}C^3H_2O_2\\H_2\end{matrix}O_2\right)$ being the first two products of the oxidation.

319. An aqueous solution of alloxan decomposes on keeping, but more rapidly on boiling, into alloxantin, parabanate, and carbonic acid—

$$\underbrace{(C^4H_2N_2O_4)_3}_{\text{Alloxan.}}=\underbrace{C^8H_4N_4O_7}_{\text{Alloxantin.}}+\underbrace{C^3H_2N_2O_3}_{\text{Parabanate.}}+CO_2.$$

Alloxantin can also be obtained by the action of sulphuretted hydrogen in the cold on an aqueous solution of alloxan—

$$2\,C^4H_2N_2O_4+H_2S=C^8H_4N_4O_7+H_2O+S.$$

Hydric nitrate easily reverses this action and oxidizes alloxantin, with formation of alloxan.

A dialurate ($C^4H_4N_2O_4$) is formed by the reduction of alloxantin by sulphuretted hydrogen, or by sodium-amalgam. It can also be obtained by adding baryta-water to a solution of alloxantin, and boiling the violet precipitate which is first formed. The baric alloxanate and dialurate are thus formed—

$$2\,C^8H_4N_4O_7 + H_2Ba_3O_4 = \underbrace{2\,C^4H_2BaN_2O_5}_{\text{Alloxanate.}} + Ba(C^4H_3N_2O_4)_2.$$

Alloxantin is accordingly built up of alloxan and dialurate with elimination of water—

$$\underbrace{C^4H_2N_2O_4}_{\text{Alloxan.}} + \underbrace{C^4H_4N_2O_4}_{\text{Dialurate.}} = \underbrace{C^8H_4N_4O_7}_{\text{Alloxantin.}} + H_2O.$$

By the action of oxidizing agents hydric dialurate is transformed into alloxan.

Murexide ($C^8H_8N_6O_6$) is the name given to a beautiful compound, of red colour by transmitted light, and of which the crystals have a green colour and metallic lustre when seen by reflected light.

Murexide is considered as ammonic purpurate, and is represented by the rational formula $C^8H_4(NH_4)N_5O_6$. It is formed by the action of ammonia or its carbonate on a hot solution of alloxantin or of alloxan.

It is also said to be formed by the action of ammonia upon dry alloxantin heated to 100°C.

Several other purpurates have been prepared, such as $C^8H_4KN_5O_6$, a deep red powder, and

$$Ba(C^8H_4N_5O_6)_2.$$

320. It appears from the elaborate investigations of Baeyer that the dialurate and alloxanate are products of oxidation of a hydric salt of the composition $C^4H_4N_2O_3$,

which he calls barbiturate. That able chemist represents dialurate as barbiturate, in which an atom of hydrogen is replaced by (H O), as seen by the formula—

$$C^4 H_3 (H O) N_2 O_3;$$

and the alloxanate will then be $C^4 H_2 (H O)_2 N_2 O_3$.

The amide of ammonic cyanate ($(C N) N H_2$) may be represented as the hydride of a radical ($(C N_2 H) H$), and if this radical replace one atom of hydrogen in a molecule of barbiturate, we have the formula—

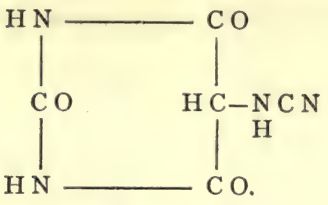
$$C^4 H_3 (C N_2 H) N_2 O_3 = C^5 H_4 N_4 O_3,$$

containing the elements of the urate.

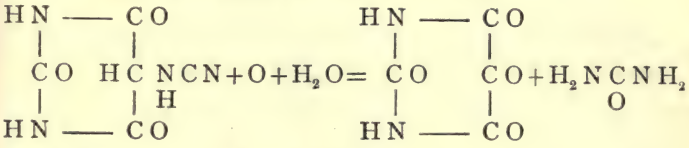
Allantoine ($C^4 H_6 N_4 O_3$) is a compound which crystallizes in transparent prisms, and was named from its occurrence in the allantoic fluid of cows. It is formed by the action of plumbic peroxide on hydric urate. Water containing the urate in suspension is heated to the boiling-point, and the peroxide is thrown into the mixture in small quantities as long as it continues to lose its brown colour. The liquid thus obtained is filtered, treated with sulphuretted hydrogen, and evaporated to crystallization. Allantoine combines with silver, forming the compound $C^4 H_5 Ag N_4 O_3$.

321. In representing the constitution of hydric urate and its derivatives by means of explicit formulæ, a line joining two atoms of carbon will stand for one-fourth of the combining power of each atom, the remaining three-fourths being saturated by some other element or elements. Similarly, a line joining an atom of carbon to an atom of any other element, means that the carbon atom is saturated by that element to the extent of one-fourth of its combining power.

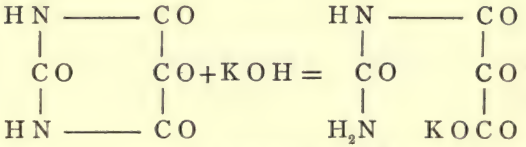
The following is the most probable explicit formula of hydric urate:—



By oxidation it forms alloxan and urea—

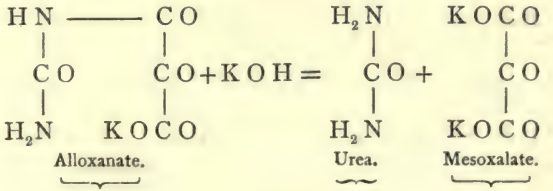


and alloxan, when boiled with a basic compound, forms an alloxanate—

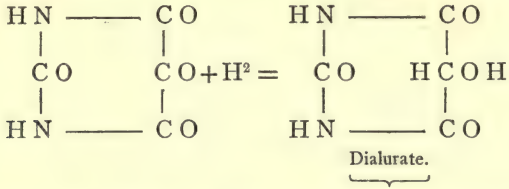


In this reaction, one of the atoms of carbon is loosened from the atom of nitrogen with which it was previously directly combined, and unites instead with an atom of (O K), while the nitrogen combines with another atom of hydrogen.

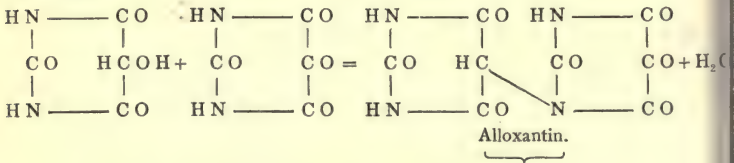
By a similar loosening of carbon from the atom of nitrogen with which it was combined, the alloxanate breaks up into mesoxalate and urea—



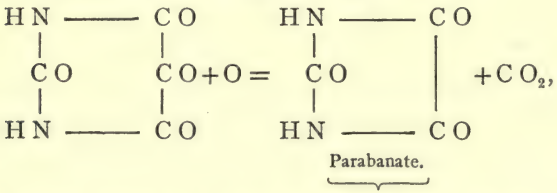
322. By the action of reducing agents, alloxan forms a dialurate—



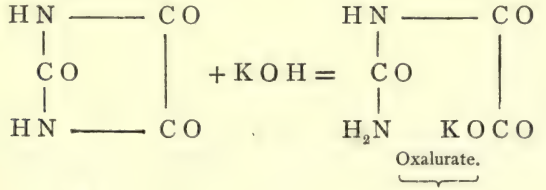
and when alloxan and dialurate are mixed, alloxantin is formed—



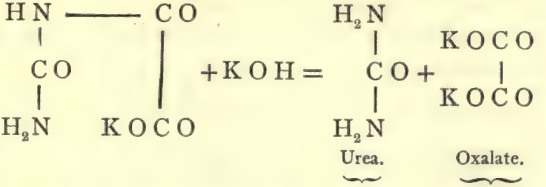
Alloxan on oxidation yields hydric parabanate—



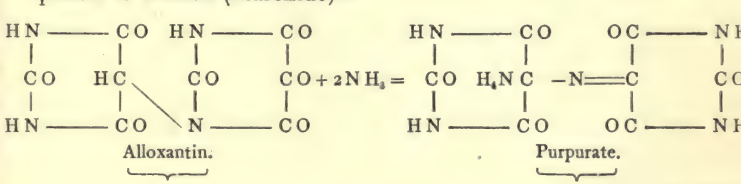
and by the action of a basic compound upon this body, an oxalurate is formed in the same way as alloxanate is formed from alloxan—



When the oxalurate is boiled, it breaks up into urea and oxalate—

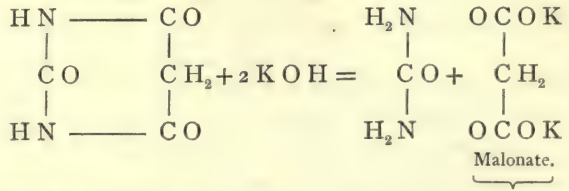


By the action of ammonia on alloxantin, ammonic purpurate is formed (murexide)—



323. Hydric barbiturate has the formula—

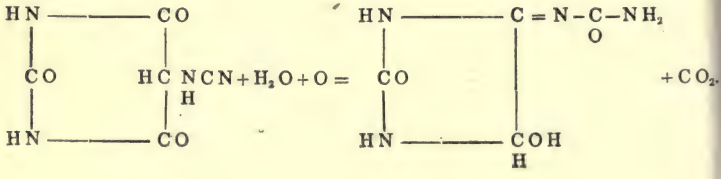
and when it is boiled with potash, it is decomposed into urea and malonate—



It will be noticed, that by replacing an atom of hydrogen

in the barbiturate by an atom of hydroxyl, dialurate is formed; and if two atoms of hydrogen be replaced by one atom of oxygen, alloxan is the result.

By the action of plumbic peroxide on hydric urate, allantoine is formed—



CHAPTER XLVIII.

324. Guanin ($C^5H_5N_5O$) is a feeble base found in guano. For its preparation guano should be boiled with milk of lime, and the solution filtered off from the residual solid matter, as often as a repetition of the process serves to dissolve out any colouring matter. Urate and guanin are thus left undissolved, while most of the other substances which accompany them in the guano are dissolved out.

Guanin dissolves in boiling hydric chloride, and can thus be separated from the greater part of the urate. It can be precipitated by ammonia from a solution of its hydrochlorate ($C^5H_5N_5OHCl$), and is insoluble in water.

By the action of a mixture of hydric chloride and potassic chlorate it is oxidized, with formation of parabanate and guanidin—

$$\underbrace{C^5H_5N_5O}_{\text{Guanin.}} + 3O + H_2O = \underbrace{C^3H_2N_2O_3}_{\text{Parabanate.}} + \underbrace{CH_5N_3}_{\text{Guanidin.}} + CO_2.$$

Guanidin (CH_5N_3) is a strong base which dissolves readily in water, and absorbs carbonic acid from the air. Its carbonate ($CO_3H_2(CH_5N_3)_2$) crystallizes from water, but is insoluble in alcohol. Its platinum-salt has the composition $PtCl_6(CH_5N_3)_2H_2$.

325. Xanthin, or xanthic oxide ($C^5H_4N_4O_2$), was found in an urinary calculus. It has since been found in flesh. It is also formed by the action of the nitrite on guanin—

$$\underbrace{C^5H_5N_5O}_{\text{Guanin.}} + NO_2H = \underbrace{C^5H_4N_4O_2}_{\text{Xanthin.}} + N^2 + H_2O.$$

It is almost insoluble in cold water, and very slightly soluble in boiling water. It combines both with hydric salts and bases, forming crystalline salts.

Another compound intimately related to xanthin in composition is

Sarkine ($C^5 H_4 N_4 O$). It is a weak base which has been found in flesh, also in blood, the liver, &c. It requires about 300 times its weight of cold water for its solution, but only 78 times its weight of boiling water. It differs in composition from hydric urate by containing two atoms of oxygen less than the urate contains, while xanthin stands between the two in composition.

A group of compounds related to the urate and to guanin by their decompositions is formed of creatine and creatinine, together with their homologues glycocyamine and glycocyamidine.

326. Glycocyamine ($C^3 H_7 N_3 O_2$) is formed by the action of glycocoll on an aqueous solution of cyanamide—

$$\underset{\text{Glycocoll.}}{C^2 H_5 N O_2} + \underset{\text{Cyanamide.}}{C N_2 H_2} = \underset{\text{Glycocyamine.}}{C^3 H_7 N_3 O_2}.$$

The compound crystallizes out from the mixture after a few days' standing. It requires 126 times its weight of cold water for its solution, but dissolves much more readily in hot water. Alcohol does not dissolve it. It forms a crystalline hydrochlorate ($C^3 H_7 N_3 O_2 H Cl$) and a platinum-salt of the composition $Pt Cl_6 H_2 (C_3 H_7 N_3 O_2)_2$.

When heated to 160°C in a current of hydric chloride, glycocyamine loses the elements of water and takes up those of the chloride. The compound thus obtained is the hydrochlorate of glycocyamidine—

$$C^3 H_7 N_3 O_2 + H Cl - H_2 O = C^3 H_5 N_3 O H Cl.$$

From this hydrochlorate the base glycocyamidine ($C^3 H_5 N_3 O$) can be liberated by plumbic oxide.

Glycocyamidine forms with zinc chloride a compound which crystallizes in needles, and is but slightly soluble in water.

327. Creatine ($C^4 H_9 N_3 O_2$) is contained in the juices of flesh. It has also been found in the brain and in urine. For its preparation lean meat should be finely minced and the soluble constituents extracted by cold water, pressure being applied to complete the separation of the fluid from the insoluble fibres. The solution thus obtained is heated to the boiling-point to coagulate the albumen contained in it, and baryta-water is subsequently added to it as long as it continues to throw down any phosphate.

After filtration, the liquid is evaporated in a water-bath, and the crystals first obtained are purified by animal charcoal.

Creatine crystallizes in clear prisms, which contain a molecule of water of crystallization. They require 74 parts of cold water to dissolve them. In absolute alcohol and in ether creatine is almost insoluble. It combines at temperatures below 33° with hydric salts, forming salts, from which it can be recovered again. But when heated to a temperature above 30°, the creatine in one of these salts gradually loses water and passes over into creatinine—

$$\underbrace{C^4 H_9 N_3 O_2}_{\text{Creatine.}} - H_2 O = \underbrace{C^4 H_7 N_3 O}_{\text{Creatinine.}}.$$

When heated with soda-lime creatine evolves methylia. The same product is formed together with ammonia by the oxidizing action of nitrate upon it. These reactions shew that the radical methyle is contained in the molecule of creatine. When boiled with baryta-water creatine takes up the elements of water, and decomposes into sarkosine and urea—

$$\underbrace{C^4 H_9 N_3 O_2}_{\text{Creatine.}} + H_2 O = \underbrace{C^3 H_7 N O_2}_{\text{Sarkosine.}} + C H_4 N_2 O.$$

And sarkosine is proved to be a methylated glycocoll ($C^2 H_4 (C H_3) N O_2$); for it has been made by the action of hydric mono-chloracetate on methylia—

$$C^2 H_3 Cl O_2 + C H_3 N H_2 = Cl H + C^3 H_7 N O_2.$$

When an aqueous solution of creatine is boiled with mercuric oxide, a compound called methyl-uramine, but which might with advantage be termed methylated guanidin, is formed, together with oxalate—

$$C^4 H_9 N_3 O_2 + O^2 = C H_4 (C H_3) N_3 + C^2 H_2 O_4.$$

Some carbonic acid is given off at the same time.

328. Creatinine ($C^4 H_7 N_3 O$) is found in the juice of flesh, and also in the human urine, as well as in the urine of horses and dogs, and especially in calves' urine.

It is also formed by the action of hot hydric salts on creatine. To prepare it from urine, calcic chloride should be added in sufficient quantity to precipitate the phosphates, &c. from the liquid previously neutralized by lime-water. The filtrate should be evaporated to crystallization, and the mother liquid from which the salts have been deposited should be mixed with a very strong solution of zinc chloride. Crystals containing creatinine combined with zinc chloride are deposited from this mixture after a few days' standing. These crystals can be dissolved in hot water, and decomposed by plumbic oxide. The solution of creatinine is finally purified by animal charcoal.

Creatinine is much more soluble than creatine in water, for at 16°C it only requires 11.5 parts of water for its solution. It dissolves still more readily in hot water, and crystallizes from a hot saturated solution in needles. Its

aqueous solution has an alkaline reaction to litmus-paper, and expels ammonia from its salts.

The platinum-salt ($Pt\,Cl_6\,H_2\,(C^4\,H_7\,N_3\,O)_2$) is soluble. The compound with zinc chloride has a composition represented by the formula $Zn\,Cl_2\,(C^4\,H_7\,N_3\,O_2)$. It is slightly soluble in water, and insoluble in alcohol.

Creatinine is converted into creatine by boiling with an aqueous alkali. Even plumbic oxide, in a boiling solution of creatinine, slowly produces the same change.

329. Glycocoll is formed by the action of ammonia on the mono-chloracetate—

$$\begin{array}{l} Cl \\ H_2C \end{array} \Big| \begin{array}{l} O \\ COH \end{array} + NH_3 = \begin{array}{l} H_2N \\ H_2C \end{array} \Big| \begin{array}{l} O \\ COH \end{array} + HCl$$

and sarkosine is methylated glycocoll; hence its explicit formula is

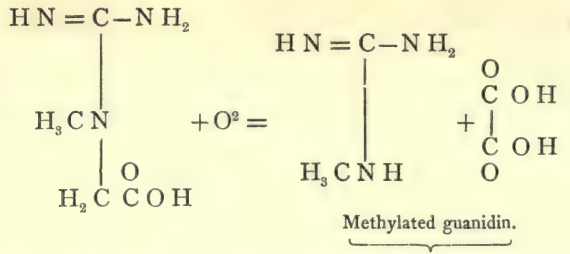
$$\begin{array}{l} H_3CNH \\ H_2C \end{array} \Big| \begin{array}{l} O \\ COH. \end{array}$$

By the action of cyanamide on sarkosine, creatine is formed, according to the equation—

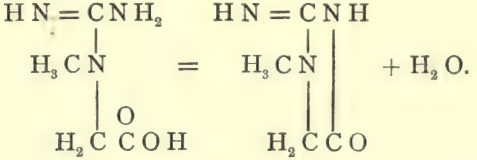
$$\begin{array}{l} H_3CNH \\ H_2C \end{array} \Big| \begin{array}{l} O \\ COH \end{array} + NCNH_2 = \begin{array}{l} HN=C-NH_2 \\ H_3CN \\ H_2C \end{array} \Big| \begin{array}{l} \\ \\ O \\ COH. \end{array}$$

Sarkosine. Creatine.

By oxidation, creatine forms methylated guanidine and hydric oxalate—



By losing the elements of water, creatine is converted into creatinine—



CHAPTER XLIX.

330. Theine ($C^8 H_{10} N_4 O_2$) and theobromine ($C^7 H_8 N_4 O_2$) are bodies of great importance as aliments. Their transformations prove that they are nearly related to the urate in constitution.

Theine is contained in tea, coffee, and in maté, or Paraguay tea, and also in a substance called guarana. It was called caffeine when first obtained from coffee, but its properties are in all respects the same, from whichever of the above-named vegetable bodies it may have been extracted.

Tea-leaves contain from two to four per cent. of theine; coffee-berries rather less than one per cent. Paraguay tea contains rather more than one per cent. of it. To prepare theine, a cold alcoholic infusion of tea-leaves is precipitated by plumbic acetate, for the removal of the tannin which is present. The excess of lead is precipitated from the filtrate by sulphuretted hydrogen; and the liquid is evaporated to crystallization. The crude product is purified by sublimation.

Theine crystallizes in long silky needles, which contain a molecule of water. It dissolves in water, alcohol, or ether. When gradually heated, it sublimes without decomposition. It combines with hydric salts, forming salts (such as the hydrochlorate $C^8 H_{10} N_4 O_2 H Cl$). Water decomposes this compound easily, and hydric chloride evaporates from it in warm air—so weak a base is the theine. The platinum-salt

($Pt\,Cl_6\,H_2\,(C^8\,H_{10}\,N_4\,O_2)_2$) is but slightly soluble in water, but the gold-salt ($Au\,Cl_4\,H\,C^8\,H_{10}\,N_4\,O_2$) is more soluble.

Oxidizing agents, such as the nitrate or chlorine, form in presence of water a compound called amalate, which is alloxantin, in which four atoms of hydrogen are replaced by four atoms of methyle: thus, $C^8\,(C\,H_3)_4\,N_4\,O_7$. The further action of the same oxidizing agents forms cholestrophane, which is in constitution dimethyl-parabanate ($C^3\,(C\,H_3)_2\,N_2\,O_3$).

When acted upon by the nitrate and subsequently by ammonia, theine yields a purple-coloured product, similar to that obtained from the urate. When boiled with potash, theine is decomposed, with evolution of methylia.

331. Theobromine ($C^7\,H_8\,N_4\,O_2$) is contained in chocolate, and is prepared from the cacao-nuts. It resembles theine in its chemical properties, and no doubt also in its action upon the human system.

An aqueous solution of theobromine mixed with ammonia is precipitated by argentic nitrate. The precipitate is a silver-salt of the composition $C^7\,H_7\,Ag\,N_4\,O_2$. By the action of methylic iodide upon this compound at 100°, Strecker has prepared theine—

$$C^7\,H_7\,Ag\,N_4\,O_2 + C\,H_3\,I = C^7\,H_7\,C\,H_3\,N_4\,O_2 + Ag\,I.$$

This reaction proves theine to be methylated theobromine.

But theobromine yields methylia by the action of various destructive reagents, and must therefore be admitted to contain the radical methyle in its molecule. The body xanthin ($C^5\,H_4\,N_4\,O_2$), described above, differs from theobromine empirically by 2 CH_2, and Strecker was led by this circumstance to prepare and examine di-methyle-xanthin—

$$C^5\,H_2\,(C\,H_3)_2\,N_4\,O_2.$$

He found it to be isomeric, and not identical with theobromine.

From these facts, it is inferred that theobromine is derived from a body of the composition $C^6 H_6 N_4 O_2$, by the substitution of methyle for one atom of hydrogen—

$$(C^6 H_5 (C H_3) N_4 O_2);$$

and that theine is similarly formed by the replacement of two atoms of hydrogen in that same body by two atoms of methyle ($C^6 H_4 (C H_3)_2 N_4 O_2$).

332. In the bile of man, of oxen, sheep, pigs, and other animals, compounds analogous to soap in their properties and constitution have been discovered. Some remarkable transformations of these compounds have been explained by Strecker's able investigations. Ox bile is the material most easily obtained in abundance for the preparation of these compounds. The liquid is usually of a brown colour, and must be used quite fresh, as it very soon undergoes putrefaction. The liquid is alkaline to test-paper from the presence of sodic salts of the acids of the bile. Dry sodic sulphate dissolves in large quantities in bile, especially with the aid of heat; and if the liquid be saturated by this salt, the original salts of the bile are precipitated in the form of a brown resinous mass, very much in the same way as a soap is precipitated from aqueous solution by the action of salt.

The solid matter obtained in this way, or by evaporating the bile to dryness in a water-bath, should be treated with alcohol, which takes up the salts of the bile and the colouring matter, leaving mucus and some mineral salts undissolved. The addition of ether to the alcoholic solution of the salts of the bile causes a precipitate; and if the precipitation of a large quantity of the solution be effected in successive steps, and each successive precipitate kept separate, it is found that all the colouring matter is carried down by the first portions precipitated, and the later portions are colourless. By redissolving these colourless precipitates in alcohol,

pouring ether on to the top of the solution, and leaving it in a closed flask, the salts of the bile can be obtained in crystals.

These crystals consist of two sodic salts which have been called by Strecker cholate and taurocholate. Each of these salts contains carbon, hydrogen, nitrogen, and oxygen; but the taurocholate contains sulphur in addition to those four elements. The proportion between these two salts varies in different sorts of bile, that from fishes being particularly rich in taurocholate. The name 'glycocholate' is applied by some chemists to Strecker's cholate, but the shorter name is preferable.

333. Sodic cholate ($C^{26}H_{42}NaNO_6$) and sodic taurocholate ($C^{26}H_{44}NaNO_7S$) dissolve readily in water, and mineral hydric salts precipitate their respective hydrogen salts.

Strong hydric sulphate added in excess dissolves the precipitate first formed in a solution of bile; and the addition of a strong syrup of cane-sugar to this hot mixture causes the appearance of a beautiful purple colour, which disappears on the subsequent addition of water. This reaction is even known as Pettenkofer's test for the salts of the bile. It belongs also to cholalates. A very characteristic and delicate test for bile is the production of a beautiful green fluorescence when a large excess of oil of vitriol is poured upon it.

Both cholates and taurocholates are decomposed by continued ebullition, in presence of an excess of baryta. The cholate takes up a molecule of water, and forms a cholalate and glycocoll—

$$\underbrace{Ba(C^{26}H_{42}NO_6)_2}_{\text{Cholate.}} + 2H_2O = \underbrace{Ba(C^{24}H_{39}O_5)_2}_{\text{Cholalate.}} + \underbrace{2C^2H_5NO_2}_{\text{Glycocoll.}}.$$

334. Taurocholate also yields cholalate, but the other product is taurine—

$$\underbrace{Ba(C^{26}H_{42}NSO_7)_2}_{\text{Taurocholate.}} + 2H_2O = \underbrace{Ba(C^{24}H_{39}O_5)_2}_{\text{Cholalate.}} + C^2H_7O_3NS.$$

Taurine had been discovered for many years, and was represented by a formula containing no sulphur, but two atoms of oxygen instead of one of sulphur. Strecker has shewn that it is the amide of ammonic isethionate, a compound formed by the combination of olefiant gas with anhydrous sulphuric acid and neutralization by ammonia—

$$\underbrace{C^2H_5(NH_4)SO_4}_{\text{Ammonic isethionate.}} - H_2O = \underbrace{C^2H_7NSO_3}_{\text{Taurine.}}.$$

The bile of hogs contains in place of cholate a salt homologous with it, which Strecker has named, from its source, hyocholate. Hyocholate is decomposed like cholate, by boiling with alkalies, and instead of cholalate it yields a salt containing CH_2 in addition to the elements of cholalate, and is called hyocholalate.

Cholesterine ($C^{26}H_{44}O$) is a beautiful crystalline body, which has been usually classed among fats, but which more recent investigations have proved to possess an alcoholic constitution. It combines with hydric stearate or benzoate like a monatomic alcohol.

CHAPTER L.

335. One of the most important groups of organic compounds are the so-called **alkaloids;** organic bases possessing powerful medical properties, and very complex molecules, of which the arrangements are for the most part unknown to us.

The most valuable alkaloid of cinchona bark is

Chinine ($C^{20} H_{24} N_2 O_2$). This bark contains this base together with cinchonine, combined as chinates.

For the preparation of chinine the bark is ground and boiled with dilute hydric sulphate or chloride. The strained liquid is precipitated by sodic carbonate, and the precipitate, consisting of chinine and cinchonine, is dissolved in dilute sulphate and crystallized, the chinine salt being first deposited. If the mixed bases be dissolved in spirits of wine, after precipitation of the original extract and desiccation of the precipitate, the cinchonine can in great part be crystallized out from the alcoholic solution, while the chinine remains in the mother liquid.

Chinine is slightly soluble in water, but it dissolves readily in alcohol or in ether. It forms crystallizable salts, of which an aqueous solution has an intensely bitter taste.

Solutions of salts of chinine, containing free hydric salts, are exceedingly fluorescent. In light containing ultraviolet rays an acid solution of the sulphate presents on its surface a beautiful blue opalescent appearance.

Ammonia and potash precipitate chinine from an aqueous

solution of one of its salts, and the precipitate is scarcely at all soluble in an excess of the precipitant.

Chlorine water acts on a solution of the sulphate in such a manner, that the subsequent addition of ammonia forms a deep emerald-green solution.

Chinine combines with hydric chloride in two proportions, forming the compounds—

$$C^{20}H_{24}N_2O_2HCl \text{ and } C^{20}H_{24}N_2O_2(HCl)_2.$$

Its platinum-salt corresponds to the latter of these compounds, for it contains its elements in the following proportions—$PtCl_6H_2C^{20}H_{24}N_2O_2$. It is but slightly soluble in water.

There are two chinine sulphates. That which usually occurs in commerce has a composition represented by the formula $SO_4H_2(C^{20}H_{24}N_2O_2)_2(H_2O)_7$. It consists of needle-shaped crystals, which dissolve very slightly in water. The crystals are gradually decomposed, and become brown, by exposure to sunshine. Dilute hydric sulphate dissolves these crystals readily, forming the hydro-chinic sulphate—

$$SO_4H_2C^{20}H_{24}N_2O_2(H_2O)_7.$$

When this salt is dissolved in strong acetate, and an alcoholic solution of iodine is gradually added to it, a compound is formed which crystallizes out from the solution in flat plates. These plates are called the sulphate of iodochinine, and are represented by the formula—

$$SO_4H_2C^{20}H_{24}N_2O_2I_2(H_2O)_5.$$

They exhibit a green colour by reflected light, and are particularly interesting from the polarizing action which they exert upon transmitted light.

Chinic Sulphate has in solution a powerful levorotatory action on polarized light. When heated to 100° C, the salt is phosphorescent.

The commercial salt sometimes contains cinchonine, and

this admixture can be discovered by adding ammonia in slight excess to a concentrated solution of acid sulphate, and then agitating the mixture with ether. Cinchonine remains undissolved.

There are two alkaloids isomeric with chinine, and formed from it. These bases are called **chinidine** and **chinicine**. They are obtained from a resinous substance called **quinoidine**.

336. Cinchonine ($C^{20} H_{24} N_2 O$) crystallizes from an alcoholic solution in the form of needles. Its solution has an alkaline reaction to test-paper. In cold water it is almost insoluble, and in boiling water very slightly soluble. The alkaloid melts at 105° C, and can be partially sublimed. Its salts exert a powerful dextrorotatory action on light. They do not give a green product when treated by chlorine and subsequently by ammonia.

There are two hydrochlorates ($C^{20} H_{24} N_2 O H Cl$ and $C^{20} H_{24} N_2 O (H Cl)_2$). The platinum-salt is represented by the formula $C^{20} H_{24} N_2 O Pt Cl_6 H_2$. There are two sulphates, viz.—

$$S O_4 H_2 (C^{20} H_{24} N_2 O)_2 \text{ and } S O_4 H_2 C^{20} H_{24} N_2 O.$$

Both chinine and cinchonine are decomposed by fusion with potash, yielding an oily product of alkaline properties, called quinoleine.

Both alkaloids unite with methylic iodide or ethylic iodide, forming the compounds—

$$C^{20} H_{24} N_2 O_2 C H_3 I \text{ and } C^{20} H_{24} N_2 O C H_3 I.$$

The methyle thus added to the composition of the base is not in the place of any typical hydrogen of ammonia, but in the place of the fourth atom of hydrogen which is added to an ammonia when an ammonium salt is formed. Freshly-precipitated argentic hydrate, added to the solution

of one of these iodides, removes the iodine and replaces it by H O—

$$C^{20}H_{24}N_2O_2CH_3I + HOAg = \\ = C^{20}H_{24}N_2O_2CH_3HO + AgI.$$

The hydrates thus obtained are very strong bases.

337. Opium is the name given to a mixture of a number of alkaloids with resins, mucilage, caoutchouc, &c., some of which occur as meconates. The substance is obtained by scratching unripe poppy capsules, and collecting, after it has dried, the milky juice which exudes. The opium undergoes a process of fermentation before it is exported for use. The proportions in which the various constituents are present vary in different specimens of opium. The best varieties, such as Smyrna opium, sometimes contain as much as fifteen per cent. of morphia, while the inferior sorts sometimes contain as little as three per cent. of morphia, or even less. Narcotine and hydric meconate can be extracted in quantities varying from six to eight per cent., and codeia, thebaia, papaverine, opianine, narceia, and meconine, are present in far smaller quantities.

338. Morphia ($C^{17}H_{19}NO_3$) is usually prepared by dissolving in water the soluble constituents of the opium, neutralizing the solution by chalk, and adding calcic chloride in quantity sufficient for the precipitation of the meconate. The alkaloids are thus left in solution as hydrochlorates, and are filtered off from the precipitate of calcic meconate, and evaporated to crystallization. The morphia hydrochlorate crystallizes out first, while the mother liquid retains a quantity of colouring matter with a little morphia and other bases. A second crystallization yields a mixture of the hydrochlorates of codeia and morphia. Morphia can be precipitated with facility by ammonia from a solution of its hydrochlorate.

Another method of preparing morphia from opium consists in boiling the aqueous extract of the drug with milk of lime, and filtering off the alkaline solution thus obtained from the undissolved matter. The morphia is combined with lime in the solution, and can be precipitated from it by the action of sal ammoniac with the aid of heat. Ammonia evaporates, while morphia falls down and calcic chloride remains in solution.

Morphia requires about 1000 times its weight of cold water for its solution, and about 400 times its weight of boiling water. The solution has an alkaline reaction to turmeric paper. Morphia dissolves readily in alcohol, but is insoluble in ether and in chloroform.

The alkaloid is readily oxidized by iodic acid or by ferric salts. Neutral ferric chloride forms with morphia a dark blue compound not very unlike ink, and this property serves as a test for morphia. Although readily soluble in fixed alkalies, morphia is but slightly soluble in ammonia.

Morphia hydrochlorate ($C^{17} H_{19} N O_3 H Cl (H_2 O)_3$) dissolves in sixteen parts of cold water, or in one part of boiling water. Its platinum-salt is represented by the formula—

$$(C^{17} H_{19} N O_3)_2 Pt Cl_6 H_2.$$

Narcotine ($C^{22} H_{23} N O_7$) is a much weaker base than morphia, as might be inferred from the larger quantity of oxygen contained in it. It is readily soluble in ether or chloroform, and can thus be separated from morphia. Narcotine is readily oxidizable, and undergoes numerous interesting decompositions, which have been ably investigated by Matthiessen and Foster. When acted on by hydric iodide in aqueous solution, a molecule of narcotine forms three molecules of methylic iodide.

339. The chief alkaloids of the Strychnos tribe of plants are **Strychnia** and **Brucia**.

These alkaloids can be prepared from the nux vomica, by

rasping the seeds and boiling them with alcohol containing one or two per cent. of sulphate. The solution thus obtained is neutralized by lime, and the alcoholic solution of the two alkaloids is evaporated to dryness. The alkaloids are subsequently dissolved in dilute nitrate, and separated by crystallization of their nitrates, the strychnia nitrate being less soluble than brucia nitrate.

Strychnia ($C^{21}H_{22}N_2O_2$) is easily precipitated by ammonia or potash from a solution of one of its salts, and is not soluble in an excess of potash. It is almost insoluble in water, or in absolutely dry alcohol. The very small quantity of it which dissolves in water, is, however, sufficient to impart a bitter taste to the liquid. Animal charcoal removes strychnia from an aqueous solution. It is readily soluble in spirits of wine, and it dissolves also in chloroform, but not in ether. Strychnia is not reddened by the action of strong hydric nitrate, and its freedom from brucia is thus tested.

When mixed with plumbic peroxide, and then moistened by strong hydric sulphate, strychnia forms a blue compound, which soon changes to a violet one, and ultimately becomes red and brown. This colour-test is used for the detection of strychnia.

The platinum-salt of strychnia is almost insoluble in water. It is represented by the formula—

$$PtCl_6H_2(C^{21}H_{22}N_2O_2)_2.$$

There is a normal sulphate of the composition—

$$SO_4H_2(C^{21}H_{22}N_2O_2)_2,$$

and an acid salt—

$$SO_4H_2C^{21}H_{22}N_2O_2.$$

Strychnia and its salts produce lockjaw, or 'tetanus,' and the alkaloid can be detected by its action on a frog, even when given in an exceedingly small quantity.

Brucia ($C^{23} H_{26} N_2 O_4$) is soluble in about 850 parts of boiling water, and in a far smaller quantity of spirits of wine. It forms large crystals containing four molecules of water. For the preparation of the pure alkaloid, its oxalate is washed with dry alcohol at 0°C. The salt is then dissolved in water, decomposed by lime, evaporated to dryness, and then crystallized from alcohol.

Strong hydric nitrate in contact with brucia produces a deep red colour, whilst methylic nitrite is evolved.

340. Nicotine ($C^{10} H_{14} N_2$) is a volatile and liquid alkaloid contained in tobacco, and imparting to that plant the narcotic properties for which its leaves are used. Nicotine is a very strong base, belonging to the class of tertiary diamines. It boils at about 250°, is readily soluble in water, and forms crystallizable salts. Its hydrochlorate is represented by the formula $C^{10} H_{14} N_2 Cl_2 H_2$.

Nicotine is exceedingly poisonous; 5 milligrammes of it placed on the tongue of a middle-sized dog having been found sufficient to kill the animal in three minutes.

CHAPTER LI.

341. A series of monatomic salts homologous with the benzoates is called the aromatic series.

Hydric Benzoate ($C^7 H_6 O_2$) is the first and most important term of the series. It is contained in gum benzoin, and is best extracted by boiling the powdered gum resin with milk of lime, filtering off the solution of calcic benzoate thus obtained, and precipitating the hydric salt from it by hydric chloride. Benzoates are present in large quantities in the putrid urine of horses and cows, and can be obtained by evaporating the decomposed urine. Fresh urine of these herbivorous animals contains no benzoate, but in its place the hippurate ($C^9 H_9 N O_3$). Hippurates break up under the influence of ferments, or of hot hydric chloride. They take up the elements of a molecule of water, forming benzoate and an amide called glycocoll —

$$C^9 H_9 N O_3 + H_2 O = C^7 H_6 O_2 + C^2 H_5 N O_2.$$

The glycocoll decomposes further in the putrefying urine.

The benzoate is a solid compound of very crystalline structure. It melts easily, and can be sublimed with very slight decomposition. It is very slightly soluble in cold water, but sufficiently so to impart to it a decidedly acid reaction. Its salts with the alkalies and alkaline earths are readily soluble in water. The study of the composition and derivatives of the benzoates has shewn that the molecule

of the hydric salt ($H\,C^7\,H_5\,O_2$) contains only one atom of hydrogen replaceable by metals.

Baric benzoate, $Ba\,(C^7\,H_5\,O_2)_2$, is not precipitated from its aqueous solution by alcohol in the presence of ammonic chloride, and this property distinguishes it from the succinate.

Potassic benzoate distilled with potassic formiate yields benzoic aldehyde, the essential oil of bitter almonds—

$$C^7\,H_5\,O\,.\,O\,K + C\,H\,O\,.\,O\,K = C^7\,H_5\,O\,.\,H + C\,O_3\,K_2.$$

The oil is thus formed by the combination of hydrogen with the radical benzoile ($C^7\,H_5\,O$).

342. When potassic benzoate is distilled by itself, a perfectly similar reaction takes place between two molecules of the salt, forming a ketone called benzophenone; one molecule furnishing phenyl, and the other furnishing benzoile—

$$C^7\,H_5\,O\,.\,O\,K + C^6\,H_5\,C\,O\,.\,O\,K = C^7\,H_5\,O\,C^6\,H_5 + C\,O_3\,K_2.$$

The analogy between benzoic hydride and benzoic phenylide is moreover not confined to the circumstances of their formation; for when they are heated with potassic hydrate, both compounds form potassic benzoate, by replacing the hydrogen of the hydrate by benzoile, while in each case this expelled hydrogen takes the place of the benzoile, forming in one case a molecule of free hydrogen (hydric hydride); in the other case, phenylic hydride—

$$C^7\,H_5\,O\,H + H\,O\,K = C^7\,H_5\,O\,.\,O\,K + H\,H;$$

$$C^7\,H_5\,O\,C^6\,H_5 + H\,O\,K = C^7\,H_5\,O\,.\,O\,K + C^6\,H_5\,H.$$

Chlorine decomposes benzoic hydride, forming benzoic chloride and hydric chloride—

$$C^7\,H_5\,O\,H + Cl\,Cl = C^7\,H_5\,O\,Cl + H\,Cl.$$

Phosphoric chloride decomposes the benzoate, forming this same benzoic chloride—

$$C^7\,H_5\,O\,.\,O\,H + P\,Cl_5 = C^7\,H_5\,O\,Cl + H\,Cl + P\,O\,Cl_3.$$

Benzoic Chloride corresponds in its general reactions to acetic chloride, and other compounds of chlorous radicals with chlorine. It reacts on potassic benzoate, forming anhydrous benzoic acid—

$$C^7 H_5 O Cl + C^7 H_5 O . O K = (C^7 H_5 O)_2 O + K Cl.$$

With potassic acetate it forms an acid, containing acetyl and benzoile in one molecule—

$$C^7 H_5 O Cl + C_2 H_3 O . O K = (C^2 H_3 O) O (C^7 H_5 O) + K Cl.$$

Benzoic ether is a fragrant oil somewhat heavier than water. It boils at 209°.

Hydric toluate ($C^8 H_8 O_2$) is obtained by the action of very dilute hydric nitrate on a hydrocarbon called cymene, or cymol. Its reactions and decompositions correspond to those of the benzoates.

The cuminate ($C^{10} H_{12} O_2$) is obtained by the oxidation of its aldehyde, which occurs in the volatile oil of cummin-seed.

Hydric Cinnamate, $C^9 H_8 O_2$, formed by the oxidation of cinnamic aldehyde, behaves like an acid of the acrylic series when fused with caustic potash, yielding potassic benzoate and acetate—

$$C^9 H_8 O_2 + 2 K O H = C^7 H_5 O . O K + C^2 H_3 O . O K + H^2.$$

It would appear to be the acrylic acid of a hydrogen salt of the benzoic series $C^9 H_{10} O_2$; which, however, is unknown.

The cinnamate is formed synthetically by the action of benzoic aldehyde on acetic chloride—

$$C^7 H_5 O H + C^2 H_3 O . Cl = C^9 H_8 O_2 + H Cl.$$

343. Benzoic Aldehyde ($C^7 H_5 O . H$) is obtained from bitter almonds, and hence commonly goes by the name of oil of bitter almonds. It does not, however, exist there ready formed, but is produced by the decomposition of a nitrogenous body called amygdaline, $C^{20} H_{27} N O_{11}$, induced

by the action of a peculiar ferment, synaptase or emulsin, in presence of water. The synaptase is found in both bitter and sweet almonds, but the amygdaline only in the bitter almonds. The decomposition of amygdaline is thus represented—

$$C^{20}H_{27}NO_{11} + 2H_2O = C^7H_6O + HCN + 2C^6H_{12}O_6,$$

three products, benzoic aldehyde, hydric cyanide, and glucose, being formed.

Benzoic aldehyde combines with oxygen, forming hydric benzoate, $C^7H_6O_2$. It also combines with hydro-sodic sulphite $HNaSO_3$. Benzoic aldehyde reacts upon ammonia, the oxygen uniting with the hydrogen of the alkali, and two atoms of nitrogen taking the place of three atoms of oxygen, a compound called **Hydro-benzamide** being formed—

$$3C^7H_6O + 2NH_3 = C^{21}H_{18}N_2 + 3H_2O.$$

Aqueous hydric chloride easily decomposes hydro-benzamide, water being taken up, and benzoic aldehyde and ammonia reproduced. By ebullition with caustic potash hydro-benzamide is transformed into an isomeric body of considerable stability. This body is called amarine. It is not decomposed like hydro-benzamide by hydric chloride, but unites with it, forming the salt $C^{21}H_{18}N_2HCl$.

Cannizzaro discovered that pure oil of bitter almonds is decomposed by alcoholic potash, forming potassic benzoate and benzoic alcohol—

$$2C^7H_6O + HOK = C^7H_5O.OK + C^7H_8O.$$

This alcohol contains the radical C^7H_7 in the place of one atom of hydrogen of water, according to the formula $(C^7H_7)OH$, and various products containing the radical C^7H_7 have been obtained from it by processes similar to those employed for preparing the corresponding derivatives from vinic alcohol.

A higher term of the same series has been obtained from cuminic aldehyde, the essential oil of cummin-seed. Cuminic aldehyde has a composition represented by the formula $C^{10} H_{12} O$. Alcoholic potash decomposes it into potassic cuminate ($C^{10} H_{11} O . O K$) and cuminic alcohol ($C^{10} H_{14} O$).

A still higher term of this remarkable series of alcohols has been discovered by Messrs. De la Rue and Hugo Müller. It is a crystalline solid, melting at 90°, and having the composition $C^{18} H_{30} O$. It is called sycocerillic alcohol.

The essential oil of cinnamon consists of a mixture of a hydrocarbon with an aldehyde, and hydro-sodic sulphite separates the latter. In the pure state, it has the fragrant odour of cinnamon, and the composition $C^9 H_8 O$. It differs from the corresponding term of the benzoic series of aldehydes in the same way as acrolein differs from propionic aldehyde, by containing two atoms of hydrogen less. By oxidation, it forms hydric cinnamate ($C^9 H_8 O_2$).

CHAPTER LII.

344. Benzole. This important hydrocarbon was discovered by Faraday in coal-gas, and is now manufactured in large quantities from the neutral oil of coal-tar. It was also obtained by Mitscherlich by distilling an alkaline benzoate with an alkaline hydrate. Thus—

$$C^7 H_5 Na O_2 + Na O H = C^6 H_6 + Na_2 C O_3.$$

This reaction shews that benzole stands to a benzoate in the same relation in which marsh gas stands to an acetate—

$$C^2 H_3 O . O Na + Na O H = C H_4 + Na_2 C O_3.$$

Benzole is likewise formed when acetylene $C^2 H_2$ is passed through a tube heated to redness. Three molecules of acetylene thus unite to form one molecule of benzole—

$$3\, C^2 H_2 = C^6 H_6.$$

When contaminated with a small quantity of the other oils, which occur with it in coal-tar, benzole can be purified by crystallization by the aid of artificial cold. The crystals of benzole which are obtained should be rapidly pressed, so as to remove the liquid oils adhering to them. In this manner it is obtained in the form of a colourless mobile liquid of 0.85 sp. gr. at 15.5° C. It has a sweetish and not disagreeable smell. It freezes at 5.5°, and boils at about 80°. Its vapour density is 39.

Benzole ($C^6 H_6 = 2$ vols.) is insoluble in water. It dissolves fats very readily, as well as India-rubber and gutta-percha.

345. When chlorine acts upon benzole in the sunshine, the latter takes up six atoms of chlorine, forming the compound $C^6 H_6 Cl_6$; but if chlorine be passed into benzole, in which iodine is dissolved, substitution products are obtained. Thus one atom of hydrogen may be replaced by one atom of chlorine, monb-chloro-benzole being formed, $C^6 H_5 Cl$. This body is also formed by the action of phosphoric chloride on phenol ($C^6 H_6 O$). It is a colourless liquid, which boils at 138°. By the further action of chlorine, a di-chloro-benzole is formed, $C^6 H_4 Cl_2$, which melts at 53°, and boils at 171°. An isomeric di-chloro-benzole is formed by the action of alcoholic potash upon the product of the action of chlorine on mono-chloro-benzole in sunshine. It melts below 0°, and boils at 175°.

Compounds in which three, four, five, and six atoms of hydrogen are replaced by chlorine, are also known. The following is a list of these bodies:—

		Melting point.	Boiling point.
Benzole	$C^6 H_6$	5·5°	80°
Mono-chloro-benzole	$C^6 H_5 Cl$		138°
Di-chloro-benzole	$C^6 H_4 Cl_2$	53°	171°
Tri-chloro-benzole	$C^6 H_3 Cl_3$	17°	206°
Tetra-chloro-benzole	$C^6 H_2 Cl_4$	139°	240°
Penta-chloro-benzole	$C^6 H Cl_5$	74°	272°
Hexa-chloro-benzole	$C^6 Cl_6$	226°	326°

Bromine forms a similar series of substitution products.

Hydric sulphate dissolves benzole on heating, forming a body of the composition $C^6 H_5 . H S O_3$, that is, benzole in which one atom of hydrogen is replaced by the monovalent group ($H S O_3$) or ($S O_2 . O H$).

Strong hydric nitrate transforms benzole into a fragrant oil called **Nitro-benzole**. This compound is heavier than water, and has the composition $C^6 H_5 N O_2$. The reaction

is an interchange between H in the oil and NO_2 in the nitrate—

$$C^6H_6 + NO_2.OH = C^6H_5NO_2 + HOH.$$

Strong hydric nitrate, mixed with strong sulphate, effects the replacement of a second atom of hydrogen by NO_2, forming di-nitro-benzole ($C^6H_4(NO_2)_2$), a crystalline solid.

By the action of fuming hydric nitrate upon the chloro-benzoles various products are obtained, containing both chlorine and the radical NO_2. Thus there is mono-nitro-chloro-benzole, $C^6H_4ClNO_2$, di-nitro-chloro-benzole, $C^6H_3Cl(NO_2)_2$, &c.

Nitro-benzole is decomposed by sulphuretted hydrogen in presence of alcohol and ammonia, and by many other reducing agents. The two atoms of oxygen are removed and replaced by two atoms of hydrogen, forming aniline (C^6H_7N).

Benzole, as first prepared from coal-tar before crystallization, is accompanied by the hydrocarbon toluole C^7H_8. This differs from benzole by containing CH_2 more, or it may be looked upon as benzole, in which one atom of hydrogen is replaced by methyle, CH_3, forming methylated benzole. It can be formed synthetically by the action of sodium upon a mixture of methylic iodide and mono-bromo-benzole; and this proves that it is constituted as above mentioned.

Toluole forms a series of compounds similar to those of benzole. Chlorine and bromine form substitution products homologous with the chloro- and bromo-benzoles. Hydric nitrate forms nitro-toluole ($C^7H_7NO_2$); and this body, by the action of reducing agents, yields a base called toluidine (C^7H_9N), homologous with aniline.

346. Aniline (C^6H_7N = 2 vols.; boiling-point, 182°; sp. gr. 1.028) is a constituent of coal-tar. It is, however, always prepared from benzole. Nitro-benzole is first prepared by the action of the nitrate on benzole, and is reduced

by the action of a mixture of metallic iron and hydric acetate. A very small quantity of acetate is employed compared to the iron, and the mass is constantly stirred while the action is going on between these materials and the nitrobenzole. Considerable heat is evolved in the process, and aniline distils out of the mixture together with its acetate. The acetate is decomposed by an alkali, and the mixture purified by distillation.

The benzole used for the manufacture of aniline usually contains toluol, and the product is accordingly accompanied by toluidine. It has been proved that the presence of toluidine is essential to the formation of the aniline red.

Aniline is a colourless liquid of very peculiar odour. It is scarcely soluble in water, and does not change the colour of red litmus-paper. Its vapour, however, forms white fumes with a rod moistened by hydric chloride. It is gradually coloured by contact with air, and ultimately transformed into a brown resin. It decomposes ferrous and ferric salts, and many other salts of feeble bases.

It combines with hydric salts in a similar manner to ammonia, forming salts which contain the elements of aniline in addition to those of the hydrogen compound. Thus—

$$C^6H_7N + HCl = C^6H_8NCl;$$

$$2\,C^6H_7N + H_2SO_4 = (C^6H_8N)_2SO_4.$$

Nearly all of its salts are soluble in water. They impart a yellow colour to fir-wood or to elder-pith. The compounds and derivatives of aniline have been chiefly investigated by Hofmann, and his researches have been fruitful of many important results.

347. Aniline is proved to be an ammonia in which one atom of hydrogen is replaced by phenyl, and in systematic nomenclature it is accordingly termed phenylia, according to the formula $C^6H_5\,H\,H\,N$. Like ethylia, it is found to

have two atoms of typical hydrogen in its molecule, as these two only can be replaced by ethyle or methyle, &c., forming ammonias, such as phen-ethylia ($C^6 H_5 C^2 H_5 H N$), phen-diethylia ($C^6 H_5 (C^2 H_5)_2 N$), phen-eth-methylia ($C^6 H_5 C^2 H_5 C H_3 N$), &c.

Its hydrochlorate yields by double decomposition with silver-nitrite an aniline nitrite, which immediately breaks up into phenilic hydrate, nitrogen, and water—

$$C^6 H_8 N N O_2 = C^6 H_6 O + H_2 O + N^2.$$

Compounds in the type of ammonic chloride have also been obtained from aniline by the process which was described above as applying to triethylia, &c. Thus di-eth-phenylia combines with ethylic iodide, forming tri-eth-phenylic iodide—

$$C^6 H_5 (C^2 H_5)_2 N + C^2 H_5 I = C^6 H_5 (C^2 H_5)_3 N I.$$

Chlorine reacts violently on aniline, forming products of substitution. Three of these have been obtained by various processes—viz. chloraniline ($C^6 H_6 Cl N$), a weaker base than aniline itself; di-chloraniline ($C^6 H_5 Cl_2 N$), a body endowed with the feeblest basic properties; and tri-chloraniline, which is incapable of combining with hydric salts. There are similar products containing bromine.

Aniline and its homologue toluidin have become important articles of manufacture for the preparation of the magnificent and varied dyes derived from them. Aniline had long been known to yield a blue colour when acted on by a hypochlorite, but the isolation of the gorgeous compounds which constitute the aniline dyes has certainly been one of the most remarkable applications of science to industrial art.

348. Aniline red or **Rosaniline** is usually made by the action of hydric arseniate on a mixture of toluidine and aniline. Its formula ($C^{20} H_{19} N^3$) shews it to be a triamine.

Its acetate ($C^{20} H_{19} N^3 C^2 H_4 O_2$) crystallizes in magnificent crystals, shewing a greenish metallic lustre by reflected light. Its hydro-chlorate ($C^{20} H_{19} N^3 H Cl$) crystallizes in needles. Rosaniline may be considered as formed by the abstraction of three molecules of hydrogen from two molecules of toluidine and one of aniline—

$$2 C^7 H_9 N + C^6 H_7 N + O_3 = C^{20} H_{19} N^3 + 3 H_2 O.$$

Aniline blue ($C^{20} H_{16} (C^6 H_5)_3 N^3 H Cl$) is made by the action of aniline on the acetate of rosaniline. Ammonia is given off in the process, and three atoms of hydrogen are replaced in the red compound by three atoms of phenyl. The product acquires its characteristic blue colour by combination with hydric chloride.

Chrysaniline ($C^{20} H_{17} N^3$) is the name given to a yellow compound, formed simultaneously with rosaniline by the action of the arseniate on commercial aniline. It is extracted from the residues from which the rosaniline has been separated.

Another beautiful dye is the so-called **mauveine** ($C^{27} H_{24} N^4$), which was discovered by Mr. Perkin, by the action of potassic dichromate on sulphate of aniline, and which opened the field of investigation of these coloured derivatives of aniline and toluidine.

349. An exceedingly important body, which in its general properties bears some resemblance to the monatomic alcohols, is the crystallizable principle of coal-tar creosote, often called carbolic acid. It also goes under the names phenylic alcohol and phenylic hydrate, but its best name is phenol.

Phenol ($C^6 H_5 O H$; boiling-point, 188°). Pure coal-tar creosote consists chiefly of this compound, and by fractional distillations it is separated from the moisture and cresol which accompany it. It crystallizes in needles, which are said to melt at 35°.

Phenol is very slightly soluble in water, but sufficiently so to impart to it the peculiar odour of creosote, and the property for which that body is remarkable — of arresting putrefaction or fermentation. Phenol dissolves in aqueous potash, forming the compound $C^6 H_5 O K$ (potassic phenilate).

Chlorine acts very violently upon phenol, forming hydric chloride and products of substitution of chlorine for the hydrogen of the phenol, such as mono-chloro-phenol, $C^6 H_4 Cl . O H$, di-chloro-phenol, $C^6 H_3 Cl_2 . O H$, &c. Bromine acts in like manner.

The action of hydric nitrate on phenol is exceedingly energetic. It consists in forming water, and replacing hydrogen in the phenol, atom for atom, by $N O_2$. The most important of the products thus obtained is tri-nitro-phenol or carbazotic acid, $C^6 H_2 (N O_2)_3 O H$, a compound which has been obtained not only by this process, but also by the action of hydric nitrate on indigo and a great number of other organic bodies.

350. Carbazotic Acid crystallizes from water in bright yellow crystals. Its potash salt ($C^6 H_2 (N O_2)_3 O K$) is very slightly soluble in water. The acid is used as a yellow dye.

Nitro-phenol, $C^6 H_4 (N O_2) O H$, and di-nitro-phenol, $C^6 H_3 (N O_2)_2 O H$, have also been obtained.

There is no doubt that these various products of substitution, formed from phenol by the replacement of part of its hydrogen by chlorine or chlorous atoms, such as $(N O_2)$, must be more strongly acid than phenol itself.

Phosphoric chloride forms phenilic phosphate $(C^6 H_5)_3 P O_4$, and at the same time phenilic chloride ($C^6 H_5 Cl$), by its action on phenol. Phosphorous chloride forms, among other products, the hydrocarbon $C^6 H_6$ benzole.

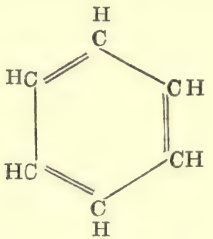
The resemblance of the reactions of phenol to those of

alcohols has led chemists to designate it frequently by the name phenilic alcohol, and to represent it by the formula C^6H_5OH. It, however, forms no aldehyde, and upon the theory of its constitution, which will be given afterwards, no aldehyde is conceivable. Hence it does not belong to the class of true alcohols, but rather to a distinct class, termed the phenols.

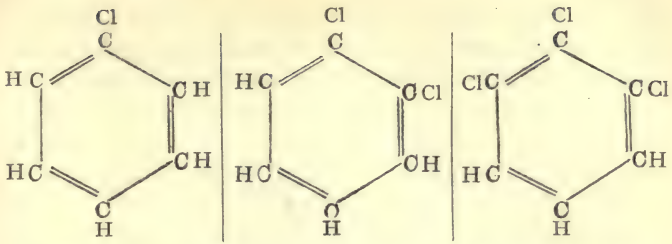
CHAPTER LIII.

351. All the aromatic bodies may be represented as formed from benzole, by substitution of the hydrogen by various elements or radicals, and thus it is important at first to understand the constitution of that important body.

The six atoms of carbon may be represented as united alternately by one and two-fourths of their combining power. The following formula will represent this explicitly, if each line joining two carbon atoms stand for one-fourth of the combining power of each carbon atom:—

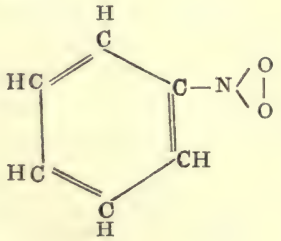


Thus each atom of carbon is united to adjacent atoms of carbon by three-fourths of its combining power, the remaining fourth being saturated by hydrogen, or some other monovalent element or radical. If one atom of hydrogen be replaced by chlorine, we get mono-chloro-benzole; if two atoms of hydrogen are replaced, di-chloro-benzole is obtained, and so on.

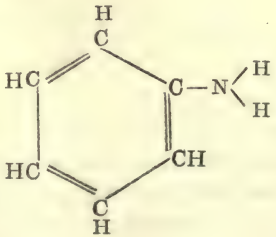


The bromo-benzoles are represented in the same manner.

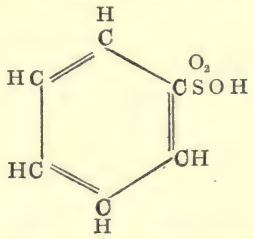
Nitro-benzole consists of benzole in which an atom of hydrogen is replaced by the group NO_2. By the action of reducing agents, two atoms of oxygen are replaced by two atoms of hydrogen, and this anomaly is best explained by the supposition that the two atoms of oxygen in nitro-benzole are united to one another by half their combining power, forming a divalent radical $(O^2)''$. Thus the formula for nitro-benzole is—



and that of aniline—



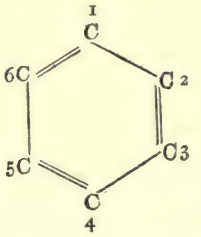
The so-called sulpho-benzolic acid, or benzole-sulphonic acid, formed by the replacement of an atom of hydrogen in benzole by the group ($S O_2 . O H$), has this constitution—



and it is seen to differ from sulphi-vinic acid ($C^2 H_5 . H S O_3$) by the fact that the atom of sulphur in the former is directly united to the atom of carbon, while in the latter it is united to it by means of an atom of oxygen—

$$H O S O C^2 H_5 .$$

352. In the formula for mono-chloro-benzole only one body is conceivable, but in di-chloro-benzole there is the possibility of three isomeric bodies. This isomerism depends upon the relative position of the two atoms of chlorine, as will be seen if the atoms of carbon be numbered—

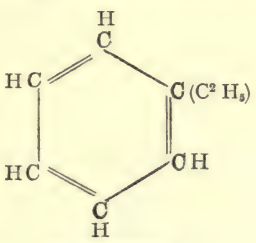


One modification is produced when the two atoms of chlorine occupy the positions 1 : 2 or 1 : 6, since in either case they are united to adjacent atoms of carbon. A second modification is formed when the atoms of chlorine occupy

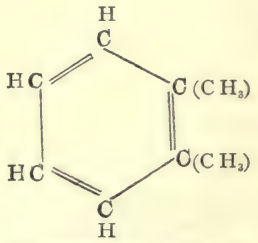
the positions 1 : 3 or 1 : 5; and a third modification is produced when the atoms of chlorine occupy the positions 1 : 4.

Tri-chloro-benzole will also have three isomeric modifications, in which the chlorine atoms will occupy the positions 1 : 2 : 3, 1 : 2 : 4, and 1 : 3 : 5 respectively.

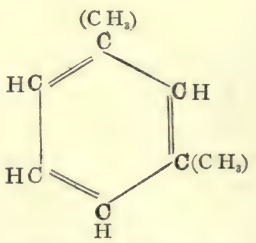
The homologues of benzole are formed by the replacement of hydrogen of benzole by alcohol radicals. Thus toluole, C^7H_8, is formed by the replacement of an atom of hydrogen by an atom of methyle, and hence there can be no isomeric modifications. In the formula C^8H_{10}, however, no less than four modifications are possible, as will be seen from the following formulæ—



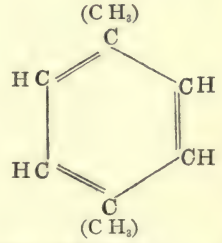
Ethyle-benzole.



Di-methyle-benzole (1 : 2).



Di-methyle-benzole (1 : 3).



Di-methyle-benzole (1 : 4).

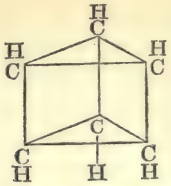
In the above formulæ there are two kinds of isomerism, firstly, due to a difference in the radicals introduced, and secondly, to a difference in position.

Benzoic acid is represented as derived from benzole by the replacement of one atom of hydrogen by the group (C O . O H). It is evident that the existence of an aldehyde corresponding to this is possible, benzoic aldehyde being thus represented C^6H_5 . (C O . H). By the hydrogenization of this aldehyde, benzoic alcohol is formed $C^6H_5(CH_2.OH)$.

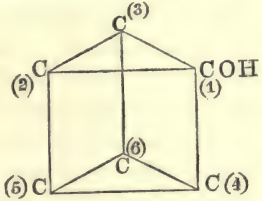
353. The formula of phenol is C^6H_5 . O H, that is a molecule of benzole in which one atom of hydrogen is replaced by an atom of hydroxyl. Phenol has often been termed an alcohol, but if it were similar in constitution to the alcohols it ought to form an aldehyde, whereas none is known, nor is one conceivable. When compared with ethylic alcohol, the cause of this is seen, for in the latter, H_3CCOH, the atom of carbon to which hydroxyl is
H_2
united is also combined with two atoms of hydrogen, and when it is oxidized these two atoms of hydrogen are removed, and the other atom of hydrogen combined directly with the carbon. In phenol this is not possible, as the carbon has only one-fourth of its combining power to be saturated. Similarly, no body corresponding to hydric acetate is possible.

The various substitution products of phenol are represented in a similar manner to those of benzole. Thus there are mono-chloro-phenol, di-chloro-phenol, &c. In mono-chloro-phenol there are three isomeric modifications possible, similar to those of di-chloro-benzole. In di-chloro-phenol there may be as many as six isomers, although it is not always possible to indicate the exact position of the elements or radicals in any given compound.

354. The following formula for benzole has been proposed, and it has the advantage over the ring formula of representing the atoms in space, and not confined to one plane.



All the isomeric derivatives of benzole can be represented equally well by this formula as by that first given. If each atom of carbon be numbered, the nature of the isomerism can be easily traced. For example, take mono-chlorophenol, and let the atom of hydroxyl be united with the



first atom of carbon, three isomeric modifications will be formed, according as the atom of chlorine is combined directly with (2) or (3), with (4), or with (5) or (6). The cause of this difference is easily seen. Calling (1) a primary carbon atom, (2) (3) and (4) secondary (because they are united directly to the primary carbon atom), and (5) and (6) tertiary carbon atoms, being only indirectly united with the primary carbon atom, (2) and (3) are each united to a primary, secondary, and tertiary carbon atom, (4) is united to primary and two tertiary carbon atoms, and (5) and (6) are each united to two secondary and one tertiary carbon atom. This explains the isomerism due to difference of position; that due to differences in the radicals introduced is explained as in the previous formula.

CHAPTER LIV.

355. Naphthalene ($C^{10} H_8$) presents great similarity to benzol, from which it differs in composition by the increment $C^4 H_2$. It is the second term of a series, benzol being the first, the members of which differ from one another by the increment $C^4 H_2$, or a multiple of it. It is formed by the destructive distillation of many organic bodies, and is found most abundantly in the oils of coal-tar, which have a high-boiling point, from which it is extracted by pressing out the liquid portions and crystallizing the residue from alcohol. Naphthalene thus obtained appears in the form of large colourless plates, which melt at 80° C, and boil at 218° C; sp. gr. at 15° C = 1.15. When fused, it has the property of absorbing a large quantity of air, which is given off on solidification.

Chlorine forms by direct addition the bodies naphthalene di-chloride ($C^{10} H_8 Cl_2$), and tetra-chloride ($C^{10} H_8 Cl_4$). It also forms substitution compounds, such as mono-chloro-naphthalene ($C^{10} H_7 Cl$), di-chloro-naphthalene ($C^{10} H_6 Cl_2$), &c. Bromine forms similar compounds. Isomeric modifications exist, as with the chloro- and bromo-derivatives of benzol.

Hydric sulphate acts upon naphthalene in the same way as upon benzol, replacing one atom of hydrogen by the group ($S O_2 . O H$). There are two modifications, known as α- and β- naphthalene-sulphonic acids. They are separated

from one another by the lesser solubility in water of the β-lead-salt.

Dilute hydric nitrate oxidizes naphthalene, forming hydric phthalate ($C^8H_6O_4$) or ($C^6H_4(CO_2H)_2$). Hydric nitrate also forms substitution products, the hydrogen in naphthalene being replaced by the group (NO_2). Thus there are the compounds nitro-naphthalene ($C^{10}H_7NO_2$), di-nitro-naphthalene ($C^{10}H_6(NO_2)_2$), and tri-nitro-naphthalene ($C^{10}H_5(NO_2)_3$). By the action of zinc and hydric chloride upon nitro-naphthalene, the hydrochlorate of naphthylamine is obtained ($C^{10}H_7NH_2.HCl$), just as aniline is formed under similar circumstances from nitro-benzol.

356. Naphthylamine is scarcely soluble in water, but easily so in alcohol. It crystallizes in colourless needles, which melt at 50°, and boil at 300°.

By the action of many oxidizing agents upon naphthylamine, a violet-red colouring matter is formed, which is soluble in boiling alcohol, crystallizing therefrom in needles having a green colour and metallic lustre. This body is the hydro-chlorate of a base, formed from naphthylamine in the same manner as rosaniline is formed from aniline, having the composition ($C^{30}H_{21}N_3$).

The hydrogen in naphthylene can be replaced by alcohol radicals, by the action of sodium upon a mixture of the alcoholic bromide and mono-bromo-naphthaline.

Hydric naphthoate ($C^{10}H_7.CO_2H$), corresponding to hydric benzoate, is formed by the action of potash upon cyano-naphthalene ($C^{10}H_7.CN$)—

$$C^{10}H_7CN + H_3KO_2 = C^{10}H_7CO_2K + NH_3.$$

There are two modifications of this body, called respectively α- and β- naphthoate. α- naphthoate crystallizes in needles, which melt at 160° C; while β- naphthoate melts at 182°.

357. Naphthol ($C^{10}H_7.OH$) is a compound analogous

to phenol. It is formed by the action of potash upon the lead-salt of one of the naphthalene-sulphonic acids. There are two modifications, one formed from each variety of the sulpho-acid. *α*- naphthol melts at 94°, and boils at 280°; *β*- naphthol melts at 122°, and boils at 290°.

Heated with caustic potash, naphthol, like phenol, combines with it, forming the compound ($C^{10}H_7 . OK$).

Hydric nitrate does not act upon naphthol directly, but di-nitro-naphthol $C^{10}H_6(NO_2)_2O$ may be obtained by the action of the nitrate upon naphthol in the nascent state, as in the decomposition of di-azo-naphthalene. It forms beautiful yellow crystals, melting at 138°, insoluble in water, slightly soluble in alcohol, ether, and benzol. It forms salts, such as the silver salt ($C^{10}H_5(NO_2)_2O.Ag$). It is used as a dye, giving to silk and wool all shades of yellow without the use of a mordant. Phosphoric chloride acts upon naphthol forming naphthylic phosphate ($PO_4(C^{10}H_7)_3$).

358. Anthracene ($C^{14}H_{10}$) is a hydrocarbon, derived, like benzol and naphthalene, from coal-tar, being found in the oils of higher boiling-point than naphthalene, and separated by repeated crystallizations. It can be formed artificially by heating chloride of benzyl (C^7H_7Cl) with water to a high temperature. It crystallizes in tables, which, when pure, have a beautiful blue fluorescence. The crystals melt at 210°–212°, and boil at about 360°.

Chlorine and bromine form substitution compounds, such as di-chlor-anthracene ($C^{14}H_8Cl_2$), tetra-chlor-anthracene ($C^{14}H_6Cl_4$), di-brom-anthracene ($C^{14}H_8Br_2$), &c.

Hydric sulphate forms the compound ($C^{14}H_9 . HSO_3$), anthracene-sulphonic acid. By the action of hydric sulphate and potassic dichromate, anthracene is converted into anthraquinone ($C^{14}H_8O^2$). Bromine replaces two atoms of hydrogen in this body, forming di-brom-anthraquinone. Similarly, boiling hydric sulphate replaces two atoms of

hydrogen by two atoms of the group ($S O_3 H$), forming di-sulpho-anthra-quinonic acid. By heating with caustic potash, the two atoms of bromine or the two of ($H S O_3$) are replaced by two atoms of hydroxyl, the natural colouring matter alizarine ($C^{14} H_6 (O H)_2 O^2$) being formed, identical with that obtained from madder.

Heated with zinc-dust, alizarine is reduced to anthracene.

CHAPTER LV.

359. Amongst organic compounds there are two important colouring bodies which deserve some study, viz. indigo and alizarine.

Indigo (C^8H_5NO) is manufactured in India by macerating the indigo plants with water in large vats. A process of fermentation takes place, by which indigo-white is formed and dissolved by the water. As soon as the process is judged to be complete, the water is pressed out from the plants and led into vats, in which air has access to it, and precipitates indigo-blue from the solution. The process is aided by beating the surface of the liquid with flat shovels, whereby more of the liquid is brought into contact with air, and the precipitate is rendered more dense.

The indigo-blue which is collected in this manner contains various earthy and other impurities, sometimes in large quantity. Good specimens contain 50 to 60 per cent. of indigo, besides substances called indigo-gluten, indigo-red, indigo-brown, and other resinous bodies. Some of these foreign bodies can be dissolved out by the successive action of dilute sulphate, boiling water, and alcohol; but the indigo-vat affords the best means of purifying the colouring-matter. There are various sorts of so-called indigo-vat, but the operation in all of them consists in transforming the indigo-blue, by the action of a reducing agent, into indigo-white, and dissolving this indigo-white. Water with lime and ferrous sulphate is a mixture which forms a 'vat' of frequent use.

The ferrous oxide becomes converted into ferric oxide, whilst the indigo is reduced and dissolved. Air should be excluded during the operation.

From the solution formed in the vat indigo-white can be precipitated by hydric chloride; or indigo-blue by the absorption of oxygen from the air.

Indigo-blue ($C^8 H_5 N O$) is a neutral solid, presenting a coppery lustre by reflected light. When heated it melts, and a small quantity can be sublimed in the form of crystals. Several oxidizing agents—such as chromic acid—are capable of converting indigo into isatine ($C^8 H_5 N O_2$). By further oxidation by strong nitrate this is in its turn converted into Nitrosalicylate ($C^7 H_5 (N O_2) O_3$), and ultimately into carbazotate ($C^6 H_3 (N O_2)_3 O$).

Indigo is decomposed by strong aqueous potash, with the aid of heat, forming, according to Gerhardt, a product of oxidation, isatate; and by simultaneous reduction of another portion, indigo-white—

$$3\,C^8 H_5 N O + H_3 K O_2 = \underbrace{C^8 H_6 K N O_3}_{\text{Potassic isatate.}} + \underbrace{C^{16} H_{12} N_2 O_2}_{\text{Indigo-white.}}.$$

When melted with potash, it evolves hydrogen, and potassic anthranilate ($C^7 H_6 K N O_2$) is formed. When distilled with potash, indigo yields aniline.

360. Alizarine ($C^{14} H_8 O_4$) = ($C^{14} H_6 (O H)_2 O^2$) is a valuable dye obtained from madder-root. Some alizarine is found ready formed in the roots, but more of it is obtained by the decomposition of a yellowish compound which is present in the root. This yellowish compound can be extracted by cold water (alizarine is not soluble in it), and the solution can be used for dyeing with alizarine colours. Alizarine dissolves in alkalies, or alkaline carbonates, forming purple solutions, from which it is precipitated on the addition of a hydric salt.

It dissolves in alcohol or ether, and also in strong sulphate, from which it is thrown down again by water. By ebullition with nitrate it is oxidized, forming phthalate and oxalate.

$$\underbrace{C^{14}H_8O_4}_{\text{Alizarine.}} + 2\,H_2O + 5\,O^2 = \underbrace{C^8H_6O_4}_{\text{Phthalate.}} + (C^2H_2O_4)_3.$$

Alizarine crystallizes in red prisms, which can be volatilized at 215°. The artificial formation of alizarine has already been described.

361. Orceine ($C^7H_7NO_3$) is a red colouring-matter which is obtained from litmus. It is made by exposing orcine to the simultaneous action of ammonia and air.

Orceine is very slightly soluble in water or ether, but alcohol dissolves it readily. It dissolves in aqueous potash or ammonia.

Orcine ($C^7H_8O_2$) is made by boiling erithrine with milk of lime for several hours. The liquid is filtered, deprived of the lime in it by hydric oxalate, and reduced to a small bulk. The orcine is dissolved in alcohol, and crystallized from that solution, and subsequently from solution in ether. The reaction gives rise to the formation of orsellate and erithrite—

$$\underbrace{C^{20}H_{22}O_{10}}_{\text{Erithrine.}} + (H_2O)_2 = \underbrace{(C^8H_8O_4)_2}_{\text{Orsellate.}} + \underbrace{C^4H_{10}O_4}_{\text{Erithrite.}}.$$

Orsellate breaks up subsequently into carbonic acid and orcine.

Orcine crystallizes with a molecule of water, which is given off at 100°. At a high temperature it can be sublimed without decomposition.

362. Turpentine ($C^{10}H_{16}$) is a member of a very numerous family of hydrocarbons which occur in plants, and often impart to them their peculiar smell. They are classed

among essential oils; of which several (such as gaultheria oil, oil of cinnamon, &c.) have already been described. Many plants supply hydrocarbons isomeric with oil of turpentine. Among the most important of these isomeric hydrocarbons may be mentioned oil of lemons, oil of bergamot, oil of birch, oil of camomile, oil of carraway, oil of juniper, oil of ginger, oil of hops, oil of parsley, oil of pepper, and oil of thyme.

These essential oils are frequently prepared by distilling the plants, or parts of plants containing them, with water. The oils are carried over into a receiver by the steam, at a temperature far below their own boiling-points. Many of them are, however, altered by exposure to the temperature of 100°, and deteriorated as perfumes. These are accordingly collected at the atmospheric temperature by placing a considerable surface of some inodorous fat in a suitable box near to the flowers which are exhaling the fragrant oil. The fat absorbs and dissolves it with its original properties.

Commercial turpentine varies considerably in its properties, according to the plant from which it was collected; but in addition to a hydrocarbon of the composition $C^{10}H_{16}$, it always contains a resinous body formed by the oxidation of that hydrocarbon. It is usually purified by rectification, the resin being left in the still. Its specific gravity is about 0.86, and it boils at 160°. Some varieties of it are dextrorotatory, some levorotatory.

A body isomeric with turpentine has been formed synthetically from the dibromide of amylene ($C^{10}H_{20}Br_2$). When this body is treated with caustic potash, rutylene ($C^{10}H_{18}$) is produced, and by combining this with bromine, and subsequent treatment with potash, terebene ($C^{10}H_{16}$) is formed.

Turpentine dissolves sulphur or phosphorus. It is also a good solvent for grease.

It is almost insoluble in water, but dissolves in alcohol or ether. It absorbs oxygen rapidly from the air, especially when mixed with litharge or ceruse.

It combines with hydric chloride, forming crystalline compounds. It also combines with water under favourable circumstances, forming crystalline hydrates.

These compounds are sometimes called artificial camphors.

Turpentine is readily oxidized by hydric nitrate, forming terebate, oxalate, and resinous bodies.

363. Camphor ($C^{10}H_{16}O$) is the common camphor of commerce. It is made from a laurel-tree, and is often called laurel-camphor. It has a density of 0.996, and it boils at 204°. It dissolves to a very small extent in water, and undergoes during the process of solution a rotatory motion. In alcohol or ether it is readily soluble, also in fixed and volatile oils.

When heated under pressure with potassic hydrate, it unites with the alkali, forming a campholate—

$$C^{10}H_{16}O + HKO = C^{10}H_{17}KO_2.$$

Anhydrous phosphoric acid deprives it of water, liberating a hydrocarbon called cymene, or, by some authors, cymol—

$$C^{10}H_{16}O - H_2O = C^{10}H_{14}.$$

When boiled with strong hydric nitrate camphor is oxidized, forming camphorate—

$$C^{10}H_{16}O + 3O = C^{10}H_{16}O_4.$$

Borneo camphor ($C^{10}H_{18}O$) is another compound which is sometimes found in commerce. It is deprived of two atoms of hydrogen by the action of nitrate, and converted into laurel-camphor. Anhydrous phosphoric acid liberates from it a hydrocarbon isomeric with turpentine.

TABLE I.

Units of heat evolved by complete oxidation of one gramme of

Hydrogen	34462°	Zinc	1330°
Charcoal.....	8080°	Iron (forming Fe_2O_3)....	1582°
Carbonic oxide	2403°	Tin	1147°
Sulphur (forming SO_2) ..	2220°	Copper	603°
Phosphorus	5747°		

TABLE II.

Specific gravity, at 14°C, *of ammonia solutions of various strengths, from Carius' determinations.*

Sp. gr.	Percent. of ammonia.	Sp. gr.	Percent. of ammonia.	Sp. gr.	Percent. of ammonia.
0.8844	36.0	0.9191	22.0	0.9556	10.0
0.8885	34.0	0.9251	20.0	0.9670	8.0
0.8929	32.0	0.9314	18.0	0.9749	6.0
0.8953	30.0	0.9380	16.0	0.9831	4.0
0.9026	28.0	0.9449	14.0	0.9915	2.0
0.9078	26.0	0.9520	12.0	0.9959	1.0
0.9133	24.0				

TABLE III.

Percentage of sulphuric acid in hydrates of various densities at 15.5°. (URE.)

Sp. gr.	Percent. of SO_3.	Sp. gr.	Percent. of SO_3.	Sp. gr.	Percent. of SO_3.
1.8460	81.54	1.6624	61.97	1.4265	44.03
1.8415	79.90	1.6415	60.34	1.4073	42.40
1.8366	78.28	1.6204	58.71	1.3884	40.77
1.8288	76.65	1.5957	57.08	1.3697	39.14
1.8181	75.02	1.5760	55.45	1.3530	37.51
1.8070	73.39	1.5503	53.82	1.3345	35.88
1.7901	71.75	1.5280	52.18	1.3165	34.25
1.7728	70.12	1.5066	50.55	1.2999	32.61
1.7540	68.49	1.4860	48.92	1.2826	30.98
1.7315	66.86	1.4660	47.29	1.2654	29.35
1.7080	65.23	1.4460	45.66	1.2490	27.22
1.6860	63.60				

SOLUTIONS TO THE PROBLEMS.

1.

A kilogramme is equal to 1000 grammes, and inasmuch as 100 parts of chlorate contain 39.183 of oxygen, 1000 grammes must contain 391.83 of the gas.

The proportion of oxygen evolved from potassic chlorate may be found by the equation which represents the decomposition, viz. $KClO_3 = KCl + O_3$; and by replacing these symbols by the weights which they respectively represent, we have $39 + 35.5 + 48$, or 122.5, parts by weight of potassic chlorate yielding 74.5 parts by weight of potassic chloride and 48 parts by weight of oxygen, whence the proportion

122.5	:	48	: :	1000	:	x
weight of $KClO_3$.		weight of O^2.		given weight of chlorate.		required weight of oxygen.

$$\therefore \quad x = \frac{48000}{122.5} = 391.83.$$

2.

In order to calculate the weight of 100 litres of oxygen we have to recollect that one volume of the gas (or 11.2 litres) weighs 16 grammes, whence the proportion

11.2	:	16	: :	100	:	x
one volume.		weight of one volume of oxygen.		number of litres given.		weight required.

$$\therefore \quad x = \frac{1600}{11.2} = 142.85 \text{ grammes.}$$

The remaining calculation is then similar to that in the last problem, viz.

39.183	:	100	::	142.85	:	x
percentage of oxygen in chlorate.				weight of 100 litres of oxygen.		weight of chlorate required.

$$\text{whence} \quad x = \frac{14285}{39.183} = 364.5;$$

$$\text{or } 48 : 122.5 :: 142.85 : x; \quad x = \frac{122.5 \times 142.85}{48} = 364.5 \text{ grms.}$$

3.

One litre of oxygen measured off at 0° becomes

$$1 + 15 \times 0.003665 = 1.054975 \text{ at } 15°,$$

and inasmuch as the contraction on cooling is equal to the expansion on heating we have the proportion

1.054975	:	1	::	30	:	x
bulk at 15° of a litre of oxygen measured off at 0°.		one litre.		measure of oxygen given at 15°.		measure required at 0°.

$$\therefore \quad x = \frac{30}{1.054975} = 28.437.$$

Using the vulgar fraction $\frac{1}{273}$, we should have the proportion

288	:	273	::	30	:	x
bulk at 15° of 273 parts of oxygen measured off at 0°.		measured at 0°.		bulk of oxygen given.		bulk required.

The 30 litres (30,000 cubic centimetres) therefore contract to 28,437 cubic centimetres.

4.

Inasmuch as the globe is to be filled with oxygen at the temperature of 12°, it will require a smaller weight of gas than if filled at 0°. The weight of a volume of oxygen at 12° can be found from the proportion

$$1 + 12 \times 0.003665 : 1 :: 16 : x; \quad \therefore \quad x = \frac{16}{1.04398} = 15.326.$$

If 11.2 litres of oxygen at 12° weigh 15.326 grammes, the weight of 13 litres of the gas is given by the proportion

$$11.2 : 15.326 :: 13 : x;$$

$$\text{whence} \quad x = \frac{13 \times 15.326}{11.2} = 17.789 \text{ grammes.}$$

Another way of finding the required weight is to calculate first what sized globe full of oxygen at 0° would contain the same weight of gas as the globe of 13 litres capacity full of oxygen at 12°. The capacity of this imaginary globe must be to that of the given globe in the same proportion as the volume of a given quantity of gas at 0° is to its volume at 12°C.

$$1 + 12 \times 0.003665 : 1 :: 13 : x;$$

$$\text{whence} \quad x = \frac{13}{1.04398} = 12.452 \text{ litres.}$$

The remaining calculation is the same as if the problem had been to calculate the weight of oxygen at 0°C needed to fill a globe of 12.452 litres capacity—

$$11.2 : 16 :: 12.452 : x;$$

$$\text{whence} \quad x = \frac{16 \times 12.452}{11.2} = 17.78.$$

5.

The first operation must be to reduce the temperature quoted in Fahrenheit's degrees, to an equivalent value on the Centigrade scale. 14°F is 18 degrees below 32°F, the freezing-point of water; and a range of 9 degrees on the Fahrenheit scale is equal to a range of 5 degrees on the Centigrade scale, so that the temperature at which the oxygen is measured off is −10°C. The rise of temperature up to 0° expands the gas in such proportion that its volume at 0° is to its volume at −10° as 1 is to 1−0.03665; i. e. as 1 to 0.96335. The further rise of temperature from 0°C to 15° expands the gas in the proportion of 1 to

$1 + 15 \times 0.003665$; i.e. 1 to 1.054975. The total rise of temperature therefore expands the gas in the proportion of 0.96335 to 1.054975.

$$0.96335 : 1.054975 :: 10 : x;$$

$$\therefore \quad x = \frac{10 \times 1.054975}{0.96335} = 10.95.$$

6.

Let the reduction for change of temperature be made first. The proportion

$$1 + 14 \times 0.003665 : 1 :: 230 : x$$

$$\text{gives} \quad x = \frac{230}{1.05131} = 218.774.$$

To reduce this volume at 740 millimetres pressure to the volume corresponding to the pressure of 760 millimetres, we have the proportion

$$38 : 37 :: 218.77 : x; \quad \text{whence } x = \frac{37 \times 218.77}{38} = 213.02.$$

7.

The volume of 43 grammes of oxygen at the normal temperature is found by the proportion

$$16 : 11.2 :: 43 : x; \qquad \text{whence} \quad x = \frac{11.2 \times 43}{16} = 30.1 \text{ litres.}$$

In order to find the volume which the gas occupies when cooled sufficiently to acquire a density of 18, we have the proportion

$$9 : 8 :: 30.1 : x; \qquad \therefore \quad x = \frac{8 \times 30.1}{9} = 26.75 \text{ litres.}$$

The temperature at which the gas will occupy this bulk is found by the proportion

$$30.1 : 26.75 :: 1 : 1 - x \; 0.003665;$$

$$\therefore \quad x = \frac{26.75 - 30.1}{.1103165} = -30^{\circ}.3.$$

8.

The required temperature is the same as if the oxygen had to be expanded in such proportion that 76 volumes became 150. The temperature necessary to do this is found by the proportion

$$1 : 1 + x \times 0.003665 :: 76 : 150;$$

$$\text{whence} \quad x = \frac{74}{.27854} = 265°.6.$$

9.

The oxygen is given at 10°C and 820 millimetres pressure. If the pressure remained constant the rise of temperature from 10°C to 300°C would expand the gas in such proportion that 1.03665 volumes would expand to 2.0995 volumes. In order to prevent any expansion the pressure must be increased in the same proportion—

$$\text{whence} \quad 1.03665 : 2.0995 :: 820 : x;$$

$$\therefore \quad x = \frac{820 \times 2.0995}{1.03665} = 1660.6.$$

From this total pressure the atmospheric pressure of 760 millimetres has to be deducted, leaving 900.6 millimetres as the height of the required mercurial column.

10.

The pressure required to compress oxygen from the density of 16 to that of 100 is found by the proportion

$$16 : 100 :: 760 : x; \quad \therefore \quad x = \frac{76000}{16} = 4750.$$

At the pressure of 4750 millimetres of mercury the weight of a litre of oxygen is found by the proportion

$$760 : 4750 :: \frac{16}{11.2} : x;$$

$$\text{whence} \quad x = \frac{16 \times 4750}{11.2 \times 760} = 8.93 \text{ grammes.}$$

The weight of chlorate required for the evolution of 8.93 grammes of oxygen is found from the proportion

$$48 : 122.5 :: 8.93 : x; \qquad \therefore \quad x = 22.8 \text{ grammes.}$$

11.

One gramme of hydrogen measures 11.2 litres at 0°C, therefore 12 grammes measure $12 \times 11.2 = 134.4$ litres at 0°. To find their volume at 15°C we have the proportion

$$1 : 1 + 15 \times 0.003665 :: 134.4 : x;$$

whence $x = 134.4 \times 1.054975 = 141.788$ litres.

12.

Assuming 11.2 litres as the volume of one gramme of hydrogen at 0°C, the volume at 12°C is 11.69 litres, and the number of grammes is found by dividing 100,000 litres by 11.69. We thus find 8554.4 grammes as the weight of the hydrogen. The volume occupied by the silk of the balloon is so small that it may be neglected, and the volume of air displaced may be taken as 100,000 litres, weighing 14.45 times as much as the hydrogen, or having

$$13.45 \times 8554.4 = 115056.68$$

grammes excess of weight over the hydrogen. If the balloon weigh 20 grammes less than this, or 115.036 kilogrammes, it will satisfy the requirements of the problem.

13.

To expand air so that it may occupy the same volume as an equal weight of hydrogen, it must be heated according to the proportion

$$1 : 1 + x \; 0.003665 :: 1 : 14.45; \qquad \therefore \quad x = \frac{13.45}{0.003665};$$

$$x = 3670°\text{C}.$$

14.

Hydrogen combines with eight times its weight of oxygen; therefore 2 grammes of hydrogen will take 16 grammes of oxygen from the cupric oxide, forming 18 grammes of water.

15.

If 11.2 litres of hydrogen weigh one gramme, 4 litres weigh 0.357. The loss of weight in the cupric oxide is eight times as great as the weight of hydrogen—

$$8 \times 0.357 = 2.856 \text{ grammes.}$$

The volume of oxygen needed is equal to that with which the hydrogen combines, viz. 2 litres.

16.

10 grammes of hydrogen measure 112 litres, and combine with 56 litres of oxygen. Assuming that air contains 20 per cent. of its volume of oxygen, 280 litres of air would be needed.

17.

Assuming that air contains 20 per cent. of oxygen (less than the truth), there will be 20 cubic centimetres of oxygen in the air employed, and these combine with 40 cubic centimetres of hydrogen, leaving 10 cubic centimetres of hydrogen mixed with 80 of nitrogen, or 90 cubic centimetres in all.

18.

10 litres of hydrogen combine with 5 litres of oxygen, and the weight of these at the normal temperature and pressure is found by the proportion

$11.2 : 16 :: 5 : x$; whence $x = 7.143$ grms. of oxygen.

The weight of chlorate requisite for the evolution of 7.143 grammes of oxygen is found by a calculation similar to those in solutions 1 and 2 to be 18.226 grammes.

19.

The heat of combustion of hydrogen is 34462°, or in other words, one gramme of hydrogen evolves in burning enough heat to warm 34,462 grammes of water from 0°C to 1°C. 20,000 grammes only have to be so warmed—

$$34462 : 1 :: 20000 : x; \quad \therefore \quad x = \frac{20000}{34462} = .580 \text{ grammes.}$$

20.

Two-thirds of the volume of the oxy-hydrogen gas, or $133\frac{1}{3}$ litres, consists of hydrogen. The weight of this is found (as in 15) to be nearly 11.9 grammes. Multiplying this number by 34462 we obtain 410097.8 as the number of grammes of water required, or 410.0978 kilogrammes.

21.

For every 102.7 volumes of ice floating in water 94 volumes of water are displaced. There are therefore 8.7 volumes of ice above water for every 94 immersed; so that the volume of ice above water is to the total bulk of the iceberg in the proportion of 8.7 to 102.7—

whence $8.7 : 102.7 :: 30000 : x$;

and $x = 3541379.3$ cubic metres.

22.

94 kilogrammes of ice measure 100 cubic decimetres, so that the bulk of 280 kilogrammes is found by the proportion

$$94 : 100 :: 280 : x; \quad \therefore \quad x = 297.8.$$

23.

At 70°C the tension of steam is found to be equal to a column of mercury 233.093 millimetres high. Its density is 9 at the atmospheric pressure of 760 millimetres, and at the given pressure its density is found by the proportion

$$760 : 233.093 :: 9 : x; \quad \therefore \quad x = 2.76.$$

It is, however, expanded by heating up to 70°, and its density at this temperature is found by the proportion

$1 + 70 \times 0.003665 : 1 :: 2.892 : x$; $\therefore$ $x = 2.2$ at 70°C.

Similar calculations shew that 12.27 is the theoretical density at 120°C.

At 140°C it is 21.26;

At 180°C it is 53.840.

24.

At 200°C the volume of steam is found by the same calculation which is employed for permanent gases, and to find its density at that temperature the proportion must be reversed; standing thus

$$1.7330 : 1 :: 9 : x; \qquad \therefore \quad x = 5.20.$$

25.

The tension of steam at 12°C is not given in our table, but from the tensions at 10°C and 15°C it may be estimated at a little over 10 millimetres.

The mixture of steam and air in the room has a total tension of 760 millimetres, and the volume of the mixture would by the removal of the steam be reduced in the proportion of 76 volumes for every 77; whence the proportion

$$77 : 76 :: 80 : x; \qquad \therefore \quad x = 78.956 \text{ cubic metres.}$$

26.

The tension of steam at 100° is 760, and this added to the tension of the air with which it mixes gives us 1520 millimetres as the measure of the tension of the moist air.

27.

In order to get one volume of steam to every two volumes of air we must have the water at the temperature at which it exerts a tension half as great as the atmospheric pressure; i. e. equal to 380 millimetres. The table shews that the temperature must be between 80°C and 85°C, and near to 82°C.

28.

100 volumes of water dissolve 1.93 volumes of hydrogen, so that 30 cubic metres dissolve 0.579 cubic metres, or 579 litres. At the normal pressure and temperature 11.2 litres of hydrogen weigh one gramme, and accordingly at 7600 they weigh 10 grammes.

$$11.2 : 10 :: 579 : x; \qquad \therefore \quad x = 517 \text{ grammes,}$$

and this weight corrected for temperature gives us 498.7 grammes.

29.

We must first ascertain the weight of oxygen given by the proportion

$$11.2 : 16 :: 4000 : x; \quad \therefore \quad x = 5714 \text{ grammes.}$$

Each kilogramme absorbs .2175° when heated 1°C, or 21.75° when heated 100°; and accordingly the four cubic metres absorb $21.75 \times 5.714 = 124.2795°$.

30.

The requisite quantity of heat must first be calculated by multiplying the rise of temperature reckoned in degrees (80) given by .4805, and the product by the number (100) of kilogrammes of steam. 3844° is the quantity of heat to be evolved by combustion of hydrogen :

$$34462 : 1 :: 384.4 : x; \quad 0.1115 \text{ kilos. is } 111.5 \text{ grms.}$$

31.

One kilogramme gives off 300×3.4046, or 1021.38°, on cooling from 300° to 0° :

90 grammes therefore give off 91.9242°.

32.

(1) Two atoms of chlorine (weighing together 71) decompose a molecule of water (weighing 18), forming a molecule of a compound (weighing 36.5), and containing one atom of chlorine combined with one atom of hydrogen; and at the same time a molecule of a compound weighing 52.5 and containing one atom of chlorine combined with one of hydrogen and one of oxygen.

(2) A molecule (weighing 208) containing an atom of barium combined with two atoms of chlorine, when added to a molecule (weighing 98) containing two atoms of hydrogen combined with one atom of sulphur and four

atoms of oxygen, is decomposed into one molecule (weighing 233) containing an atom of barium combined with an atom of sulphur and with four atoms of oxygen; and at the same time into two molecules of a compound (each weighing 36.5) consisting of an atom of hydrogen combined with an atom of chlorine.

(3) A molecule of a compound (weighing 58.5) consisting of an atom of sodium combined with an atom of chlorine, when mixed with a molecule (weighing 98) consisting of two atoms of hydrogen combined with one atom of sulphur and four atoms of oxygen, loses a molecule (weighing 36.5) of a compound of one atom of chlorine with one atom of hydrogen, and forms a molecule (weighing 120) consisting of one atom of hydrogen, one of sodium, one of sulphur, and four of oxygen.

33.

The weight of the nitrogen may be calculated on the assumption that it is measured at the normal temperature and pressure

$$11.2 : 14 :: 50000 : x = 62500 \text{ grammes.}$$

The weight of oxygen corresponding to this would be found by the proportion

$$76.9 : 23.1 :: 62500 : x;$$

but as chlorate is required we may substitute for 23.1 the weight of the salt, which contains 23.1 parts by weight of oxygen, viz. 58.94: the result is 47903 grammes of chlorate.

34.

The problem is a reduction of 20.9 cubic centimetres of oxygen and 79.1 cubic centimetres of nitrogen from 10°C and 350 millimetres to 0°C and 760 millimetres.

$$1.03665 : 1 :: 209 : x; \quad \therefore \quad x = 201.6,$$

and $76 : 35 :: 201.6 : x; \quad \therefore x = 92.84$ cubic centimetres.

Similar calculations for the nitrogen give 351.4 cubic centimetres.

35.

The tension of steam increases 3.534 millimetres: so that a cubic metre of the air saturated at 10° will gain moisture in the proportion of 3.534 volumes for every 760 original volumes; i. e. it will gain 4.65 litres of steam at 760, and 15, or 4.47 litres, at 0°, equal to 3.59 grammes.

36.

The formulæ of the compounds shew that 85 parts by weight of the sodic nitrate should yield 63 parts by weight of the hydric nitrate. A kilogramme should therefore yield 741 grammes.

37.

98 parts of the hydric sulphate decompose 2×101, or 202, of the nitrate. 500 grammes of the nitrate may therefore be decomposed by 242.5 grammes of the sulphate.

38.

According to the equation

$$3\,Cu + 8\,H\,N\,O_3 = 2\,N\,O + 3\,Cu\,(N\,O_3)_2 + 4\,H_2\,O$$

we find by substituting for the first three formulæ the weights which they respectively denote, that 3×63.5 of copper react on 8×63 of hydric nitrate to form 2×30 of nitric oxide.

$$60 : 504 :: 10 : x$$

gives for the requisite weight of nitrate 84 grammes.

And in like manner we find 31.75 grammes of copper.

39.

The equation shews that 63 parts of the nitrate form 18 parts by weight of water; so that 200 grammes form 57 grammes of water.

40.

56 parts by weight of the hydrate require 65 parts of the nitrate; so that 800 require 900 of the nitrate.

41.

A molecule of the nitrate $Pb(NO_3)_2$ evolves one atom of oxygen, or 331 parts evolve 16 parts; therefore 300 grammes evolve 14.5 grammes.

42.

The reaction is thus expressed—

$$NO + H^2 = N + H_2O,$$

$NO = 2$ vols., $H^2 = 2$ vols., $N = 1$ vol.:

so that 10 cubic centimetres of nitric oxide are required, and 5 cubic centimetres of nitrogen are liberated.

43.

The process is this,—

$$2NO + 3O + H_2O = 2HNO_3.$$

Four volumes of nitric oxide accordingly require 3 volumes of oxygen. Now 15 grammes of nitric oxide measure 11.2 litres; so that 10 grammes measure 7.46 litres, and the volume of oxygen needed is $\frac{3}{4}$ of this, or 5.595 litres.

44.

$N_2O_3H_4 = N_2O + 2H_2O$ shews that 80 parts of the salt evolve 44 of the gas; so that a kilogramme evolves 550 grammes, measuring 280 litres.

45.

N_2O occupies 2 volumes, N^2 is also 2 volumes, and O is 1 volume; so that 2 volumes of nitrous oxide yield 3 volumes of the mixture, and one litre yields $1\frac{1}{2}$ litre.

46.

The combustion is represented by the equation

$$N_2O + H^2 = N^2 + H_2O;$$

which shews that the volume of hydrogen is equal to that of the nitrous oxide. 44 grammes of nitrous oxide occupy 22.4 litres; so that 10 grammes measure 5.09 litres, and accordingly 5.09 litres of hydrogen could be burnt.

47.

At the normal temperature and pressure the gas will measure 13.176 litres. At 12° and normal pressure it measures 13.75; and the reduction for pressure brings this to 14.32 litres.

48.

$ClNH_4$ weighs 53.5 and yields NH_3, weighing 17. One kilogramme of ammonia is therefore evolved from 3147 grammes of the salt.

49.

$NH_3 = 2$ volumes, $N = 1$ volume shew us that the nitrogen occupies half as great a volume as the ammonia from which it is liberated; so that 5 cubic centimetres of nitrogen are liberated from 10 of ammonia.

50.

$NH_3 + NO_2H = N^2 + 2H_2O$ shews us that the nitrogen evolved is equal in volume to the ammonia decomposed; 17 grammes of ammonia measure 22.4 litres; so that 10 grammes occupy 13.176 litres, and 13.176 litres of nitrogen are evolved.

51.

The ammonia is in the proportion of one molecule to one of the original salt, or 17 grammes to 101 of the salts; so that 100 grammes of nitre require 16.83 of ammonia, and 79.2 of ammonic nitrate are formed.

52.

$NO + 5H = NH_3 + H_2O$ shews us that 30 grammes of the oxide form 17 of ammonia; so that 3 grammes will form 1.7 of ammonia.

53.

$N_2O_5 + 16H + 2HCl = 2NH_4Cl + 5H_2O$ shews that 108 grammes of the acid form 107 of sal-ammoniac; so that the weight of acid is $\frac{108 \times 2.14}{107} = 2.16$.

54.

The formula of the double chloride is $Pt\,Cl_6\,N_2\,H_8$, representing 446, and this weight contains 28 of nitrogen; so that 3.428 contain 0.215 of nitrogen.

55.

$C + O^2 = C\,O_2$ tells us that 12 grammes of carbon unite with 32 grammes of oxygen. Air contains 23.1 per cent. by weight of oxygen; $23.1 : 100 :: 32 : x$ gives us 138.5 kilogrammes of air as the quantity needed for the combustion of 12 kilogrammes of carbon; so that $\frac{138.5}{12}$ gives the weight of air needed for one kilogramme, viz. 11.54 in kilogrammes.

56.

500 grammes of carbon form 933 litres of carbonic acid. The room originally contained in every cubic metre 210 litres of oxygen or 12,600 litres in all. 933 litres of oxygen are consumed to form carbonic acid, leaving

11,667 litres of oxygen, mixed with
47,400 litres of nitrogen and
933 litres of carbonic acid;

corresponding to the following percentages, viz.

oxygen 19.445, nitrogen 79, carbonic acid 1.555.

57.

The equation tells us that 84 grammes of the double carbonate and 98 grammes of the sulphate evolve 44 grammes of the acid.

$$44 : 84 :: 1000 : x$$

gives us 1909 grammes of the carbonate, and a similar proportion gives 2227 grammes of sulphate.

58.

The volume of the acid is the same as that of the oxygen,

so that we have merely to calculate the volume of 100 grammes of oxygen from the well-known weight of the absolute volume; the result is 70 litres.

59.

12 grammes of carbon are contained in 22.4 litres of the acid, for $C O_2$ contains 12 grammes of carbon and measures 22.4 litres; or one litre therefore contains 0.53 grammes.

60.

$Ca C O_3$ represents 100 grammes of the carbonate and yields $C O_2$, measuring 22.4 litres. The 20 litres required at 15°C are equal to 18.95 litres at 0°C.

$$22.4 : 100 :: 18.98 : x$$

gives 84.6 grammes of carbonate.

61.

The equation $C O_2 + C = 2 C O$ represents the reaction which takes place; $C O_2$ occupies 2 volumes, 2 C O occupies 4 volumes; so that five litres of carbonic acid are needed for the formation of 10 litres of carbonic oxide.

62.

Carbonic oxide occupies twice the volume of the oxygen contained in it; so that a litre of oxygen forms 2 litres of carbonic oxide.

63.

Two volumes of carbonic oxide combine with one volume of oxygen to form two volumes of carbonic acid; so that three volumes of the mixed gases combine to form two volumes of carbonic acid, and ten litres of the mixture form $6\frac{2}{3}$ litres of carbonic acid.

64.

A ton of carbon requires $1\frac{1}{3}$ ton or 2986 lbs. of oxygen to form carbonic oxide. The weight of air containing this oxygen is found by the proportion

$$23.1 : 100 :: 2986 : x; \qquad \therefore \quad x = 12929 \text{ lbs.};$$

100 cubic inches of air weigh 32.586 grains; so that a cubic foot weighs 563 grains, and

$$\frac{12929 \times 7000}{563} = 160751$$

gives the number of cubic feet of air.

The carbonic oxide occupies twice as great a volume as the oxygen from which it is made, so that 100 cubic feet of air yield 121 cubic feet of the mixture; and we obtain 194508.71 cubic feet of the mixture. The heat evolved by the combustion of a pound of carbon to form carbonic oxide is sufficient to heat 2473 lbs. of water from 0°C to 1°C, and accordingly the ton of carbon evolves enough heat to heat 2240×2473 lbs. from 0°C to 1°C.

The heat obtainable by combustion of the carbonic oxide is $5607 \times 2240°$.

65.

One kilogramme of carbon evolves 8080°, and one kilogramme of water requires 637°; $\frac{8080}{637}$, or 12.68 kilogrammes, would therefore be evaporated.

66.

11.2 litres of carbonic oxide weigh 14 grammes; so that one litre weighs 1.25 grammes, and this weight multiplied by 2.403 gives 3.00375 degrees of heat.

67.

The formula of the crystallized salt is

$$C^2 H_2 O_4 (H_2 O)_2,$$

weighing 126 grammes, and this evolves C O, or 22.4 litres of carbonic oxide: $126 : 22.4 = 50 : x$, or nearly 9 litres.

68.

The molecule of oxalate weighs 90 units and neutralizes 34 units of ammonia, forming the salt $(N H_4)_2 C^2 O_4$. A kilogramme would neutralize 377.7 grammes.

69.

The decomposition of the oxalate is thus described:—

$$C^2 H_2 O_4 = C H_2 O_2 + C O_2;$$

90 parts of oxalate form 46 of formiate. A kilogramme therefore forms nearly 511 grammes of formiate, and 46 parts of this require 17 of ammonia, forming $N H_4 C H O_2$; so that 188.75 grammes of ammonia are required.

70.

$C H_4$ represents 22.4 litres, weighing 16 grammes; 10 litres weigh 7.14 grammes.

71.

Marsh gas requires twice its volume of oxygen for complete combustion, forming twice its own volume of steam, as seen from the equation

$$C H_4 + 4 O = C O_2 + 2 H_2 O;$$

so that a litre of the gas forms two litres of steam. Assuming the percentage of oxygen in air at 21, we find that 9.52 litres of air are needed.

72.

The molecular weight of the acetate is 98, and that of the marsh gas obtained by the action of potassic hydrate is 16. A kilogramme of acetate yields 163 grammes of gas.

73.

$C^2 H_4$ weighs 28 grammes and measures 22.4 litres. A kilogramme measures 800 litres.

74.

The combustion is represented by the equation

$$C^2 H_4 + 3 O^2 = 2 C O_2 + 2 H_2 O;$$

which shews that three litres of oxygen are needed, and that two litres of carbonic acid and two litres of steam are formed.

75.

A molecule of olefiant gas occupies two volumes, and contains four atoms of hydrogen, which in the free state occupy four volumes. A litre of ethylene would therefore yield two litres of hydrogen.

76.

$C^2 H_2 + 5 O = 2 C O_2 + H_2 O$ shews that two volumes of acetylene combine with five of oxygen, forming four volumes of carbonic acid and two volumes of steam.

A litre of oxygen would therefore burn 400 cubic centimetres of acetylene, forming 800 cubic centimetres of carbonic acid and 400 of steam.

77.

22.4 litres weigh 26 grammes. A litre, therefore, weighs 1.16 grammes.

78.

The ethylene measures one cubic metre and burns in 20.9 cubic metres of oxygen, absorbing three cubic metres of oxygen and forming two cubic metres of carbonic acid and two cubic metres of steam.

The room contains

79.1	cubic	metres	of nitrogen,
17.9	—	—	oxygen,
2	—	—	carbonic acid,
2	—	—	steam.
101	cubic	metres.	

The percentages are

nitrogen	78.317
oxygen	17.723
carbonic acid	1.980
steam	1.980

79.

$C^2 N_2$ represents 22.4 litres and 52 grammes. A litre weighs, therefore, 2.321 grammes.

80.

The equation $C^2 N_2 + 4 O = 2 C O_2 + N^2$ represents the process as requiring two litres of oxygen, and evolving two litres of carbonic acid and one litre of nitrogen; 9.57 litres of air are needed.

81.

$C O N_2 H_4$ weighs 60 and yields $N^2 H_6$, weighing 34. One gramme of urea yields $5\frac{2}{3}$ decigrammes.

82.

60 grammes of urea combine with 63 grammes of hydric nitrate, forming the compound $C O_4 H_5 N_3$. One gramme of urea yields 2.05 grammes of the nitrate.

83.

The molecule of the fulminate $Ag_2 C_2 N_2 O_2$ weighs 300, and 304 grammes of it would yield 44.8 litres of carbonic oxide and 22.4 litres of nitrogen. A gramme would yield 0.1493 litre of carbonic oxide and 0.0746 of nitrogen.

84.

The molecule of the salt is 422, and it yields three molecules of prussic acid, weighing 81; so that 500 grammes yield nearly 96 grammes of acid.

85.

10 grammes occupy 7.225 litres. The combustion is represented by the equation

$$2 C H_5 N + 9 O = 2 C O_2 + 5 H_2 O + N_2.$$

The molecule of methylia weighs 31, and 31 grammes of it require 50.4 litres of oxygen for combustion, forming 22.4 litres of carbonic acid, 56 litres of steam, and 11.2 litres of nitrogen. 10 grammes of the body require 16.26 litres of oxygen for combustion, and form

7.2258 litres of carbonic acid,
18.0645 litres of steam,
3.6125 litres of nitrogen.

86.

Hydric chloride is formed by the union of equal volumes of hydrogen and chlorine without condensation; so that a litre of hydric chloride yields half a litre of hydrogen.

87.

The molecular weight of salt (Cl Na) is 58.5, while that of hydric chloride (Cl H) is 36.5. The proportion

$$36.5 : 58.5 :: 1000 : x$$

gives 1602 grammes of salt.

88.

The equation representing the reaction by which chlorine is evolved is

$$Mn O_2 + 2\,H\,Cl = Mn Cl_2 + Cl^2 + H_2 O;$$

from which it appears that $Mn O_2$, representing 87 parts by weight of the peroxide, evolves Cl^2, or 71 parts by weight of chlorine. $71 : 87 :: 100 : x$ gives 122.5 grammes.

89.

In this process chlorine expels oxygen according to the equation $H_2 O + Cl^2 = 2\,H\,Cl + O$.

Cl^2 occupies two volumes while O occupies one volume; so that half a litre of oxygen is evolved.

90.

The reaction takes place according to the equation

$$H\,Cl + K\,H\,O = K\,Cl + H_2 O.$$

The molecule H Cl weighs 36.5, and K HO weighs 56.

$36.5 : 56 :: 100 : x$; 153.4 grammes.

91.

The molecules $N H_3$ and Cl H represent 17 and 36.5.

$36.5 : 17 :: 10 : x$; 4.66 grammes = 6.137 litres.

92.

Argentic chloride (Ag Cl) has a molecular weight of 143·5, and this is formed from 36.5 parts of hydric chloride.

$$143{\cdot}5 : 36{\cdot}5 :: 4{\cdot}53 : x; \qquad \text{whence} \quad x = 1{\cdot}106.$$

20 grammes of solution contained 1.106 of chloride, and 100 parts of the solution therefore contain 5·53.

93.

The molecule of sal-ammoniac ($N H_4 Cl = 53{\cdot}5$) occupies four volumes. A litre of its vapour therefore weighs $\frac{53{\cdot}5}{44{\cdot}8}$, or 1.194 grammes.

94.

The decomposition is expressed by the equation

$$C O Cl_2 + H_2 O = C O_2 + 2 H Cl.$$

$C O Cl_2$ occupies two volumes, $C O_2$ also occupies two volumes, and $2 H Cl$ occupy four volumes. One litre of carbonic acid and two litres of hydric chloride are therefore obtained.

95.

The combination is represented by the equation

$$C^2 H_4 + Cl^2 = C^2 H_4 Cl_2,$$

which shews that a litre of chlorine is required, and that the vapour of the compound formed measures one litre.

96.

The molecule of chloroform has the formula

$$C H Cl_3,$$

representing 119.5 parts by weight, and as this occupies two volumes, one litre weighs 5.34 grammes.

97.

Two volumes of the chloride form two volumes of carbonic acid and eight volumes of hydric chloride, so that a litre of the chloride forms a litre of carbonic acid and four litres of hydric chloride.

98.

11.2 litres (or 112,000 cubic centimetres) of bromine vapour at 0° and 760 weigh 80 grammes (or 80,000 milligrammes).

$112 : 800 :: 1 : x$ gives 7.1428 milligrammes

as the weight at 0°, and from this the weight is found at 150°C to be 4.6 milligrammes.

99.

11.2 litres of hydric bromide gas contain 40.5 grammes, or 40 grammes of bromine; so that a litre contains

$$\frac{40}{11.2} = 3.57 \text{ grammes of bromine.}$$

100.

127 grammes of iodine are required for the formation of 22.4 litres of hydric iodide.

$$127 : 22.4 :: 10 : x$$

gives 1.76 litres as the volume obtainable from 10 grammes.

101.

$Mn O_2 + 4 H Cl + 2 K I = Mn Cl_2 + 2 H_2 O + 2 K Cl + I^2$

represents the evolution of chlorine and its action on the iodide in one equation, and shews that 87 grammes of the peroxide liberate 254 grammes of iodine.

$$87 : 254 :: 6 : x$$

gives 17.5 iodine from 6 grammes.

102.

$Ca C O_3 + H_2 S O_4 = Ca S O_4 + C O_2 + H_2 O$ shews that 100 grammes of the carbonate form 136 of the sulphate.

103.

$H_2 S$ weighs 34 grammes and occupies 22.4 litres, so that one litre contains $\frac{32}{22.4} = 1.428$ grammes.

104.

$H_2S + 3O = H_2O + SO_2$ shews us that two volumes of sulphuretted hydrogen require three volumes of oxygen, forming two volumes of steam and two volumes of sulphurous acid. One cubic centimetre therefore requires 1.5 cubic centimetre of oxygen, and forms one cubic centimetre of steam and one cubic centimetre of sulphurous acid.

105.

$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$ shews that 340 grammes of antimonious sulphide are required for the evolution of 102 grammes of sulphuretted hydrogen. The proportion

$$102 : 340 :: 500 : x$$

gives 1666 grammes as the requisite weight of antimonious sulphide.

106.

The equation $S + O^2 = SO_2$ shews that the weight of sulphurous acid is double that of sulphur, so that 20 grammes are obtained corresponding to 7 litres.

107.

$SO_2 + 2KHO = K_2SO_3 + H_2O$ shews that 64 grammes of the acid react on 112 grammes of the hydrate, so that 57.1 grammes react on 100 of the hydrate.

108.

A solution of 1.5957 specific gravity is stated to contain 57.08 per cent. of acid. The equation

$$CaO + SO_3 + Aq = SO_4Ca + Aq$$

tells us that 56 grammes of lime require 80 grammes of acid, so that 10 require 14.285 grammes, and the proportion

$$57.08 : 100 :: 14.285 : x$$

gives 25 grammes of the aqueous acid.

109.

In other words, What volume of air contains one kilo-

gramme of oxygen? We may first calculate the volume of the kilogramme of oxygen. The proportion

$$16 : 11.2 :: 1000 : x$$

gives us 700 litres; and the proportion

$$20.9 : 100 :: 700 : x$$

gives the corresponding volume of air at 3349 litres.

110.

$S O_4 H_2$ occupies in the state of vapour the volume of two molecules, viz. four volumes; 98 grammes yielding 44.8 litres, so that 10 grammes yield 4.57 litres at 0°, and the expansion to 400°C gives 11.27 litres.

111.

$C S_2$ contains 12 grammes of carbon and occupies 22.4 litres, and the proportion

$$12 : 22.4 :: 100 : x$$

gives $186\frac{2}{3}$ litres as the volume at 0° obtainable from 100 grammes of carbon. At 100°C this will measure 255.08 litres.

112.

The equation $C S_2 + 3 O^2 = C O_2 + 2 S O_2$ shews that 76 grammes of the sulphide require 67.2 litres of oxygen, forming 22.4 litres of carbonic acid and 44.8 litres of sulphurous acid; so that 10 grammes require 8.84 litres of oxygen, forming 2.94 litres of carbonic acid and 5.89 litres of sulphurous acid.

113.

The equation $C S_2 + 6 N O = 3 N^2 + C O_2 + 2 S O_2$ shews us that 76 grammes of carbonic sulphide require 134.4 litres of nitric oxide; so that 10 grammes require nearly 17.7 litres.

114.

$S^2 Cl_2$ weighs 135 and occupies 22.4 litres; so that one

litre weighs a little over 6 grammes at 0°C, or 3.46 grammes at 200°C.

115.

The equation $S O_2 Cl_2 + 2 H_2 O = S O_4 H_2 + 2 H Cl$ shews that 22.4 litres of chlorosulphuric acid vapour form 44.8 litres of hydric chloride gas; so that two litres would be formed in the process described.

116.

The equation $P H_3 + H I = P H_4 I$ shews that the gases combine in the proportion of equal volumes; so that one litre of hydric iodide will be taken up.

117.

The equation $2 P H_3 + 4 O^2 = P_2 O_5 + 3 H_2 O$ represents the process, and shews that four volumes of phosphuretted hydrogen combine with eight volumes of oxygen; so that one cubic centimetre of the gas requires two cubic centimetres of oxygen.

118.

The equation $P^2 + 3 Cl_2 = 2 P Cl_3$ shews that six volumes of chlorine form four volumes of the chloride; so that one litre of chlorine forms $\frac{2}{3}$ of a litre of the chloride.

119.

The product obtained by saturation is $P Cl_5$, and this in the state of vapour occupies four volumes; 31 grammes of phosphorus form 44.8 litres of vapour; so that 10 grammes of phosphorus form nearly 14.3 litres of the vapour.

120.

The action of chlorine is according to the equation,

$$P H_3 + 4 Cl^2 = P Cl_5 + 3 H Cl.$$

Two volumes of the phosphide react on eight volumes of chlorine; one litre of the phosphide therefore takes up four litres of chlorine.

121.

The formula of boric chloride shews it to contain three atoms of chlorine in two volumes, and these three atoms of chlorine would form three molecules of hydric chloride, each occupying two volumes; so that a litre of boric chloride will form three litres of hydric chloride.

122.

Boric fluoride has the molecular formula BF_3; 11 grammes of boron are contained in two volumes or 22.4 litres; so that one litre contains 0.491 grammes of boron.

123.

The process of conversion is represented by the equation

$$SiO_2 + 4HF = SiF_4 + 2H_2O,$$

which shews us that 60 grammes of silica form 22.4 litres of the gas; 10 grammes therefore form 3.733 litres.

124.

The equation $SiCl_4 + 2H_2O = SiO_2 + 4HCl$ represents the process and shews that 170 parts of the chloride form 60 of silica, and 50 grammes of the chloride form 17.65 grammes of silica.

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